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ELECTRICITY OF THUNDERSTORMS

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Received January 28, 1952

We are living between two charged conductors. One of these conductors is the earth itself, which in fine weather shows a negative charge, which will produce on the average in the vertical direction a positive potential gradient of the order of 100 volts per metre. The other conductor is the ionosphere, which ordinarily has an excess positive charge. Under the influence of these two charged conductors, there are movements of ions, positive ions downwards, and negative ions upwards. The rate of movement of positive ions towards the earth is such as to constitute an average current of 4×10^{-16} amp./cm.^{2} over the oceans and 10^{-16} amp./cm.^{2} over land. Taking the average value of 3×10^{-16} amp./cm.^{2} for the whole earth, we get a current of 1,500 amperes for the earth as a whole, and it has been calculated that at this rate the earth's negative charge will be fully wiped out in about 40 minutes.

But this does not happen. While conditions in fine weather are on the average as indicated above, there are large variations in charges during 24 hours in any particular area over both the conductors and also during disturbed weather, namely, when a thunderstorm is in progress. Indeed the measurements of these variations in the charges on the earth's surface as well as the ionosphere are now a daily routine.

It is now becoming increasingly apparent that in the production of these variations the main contributory cause is thunderstorm. Every thunderstorm has just the type of mechanism which makes it act like a dynamo driving electricity upwards. It has been estimated that at any instant, taking the earth as a whole, there are more than 1,000 thunderstorms in progress. Collectively, therefore, they play an important role in the circulation of electricity through the atmosphere. A remarkable contribution was made in 1936 by Whipple and Scrase in regard to the part which thunderstorms play in producing the diurnal variation of the electric field of the earth. It has been observed that all over the oceans the diurnal variation occurs according to universal time and not according to local time, the maximum occurs at 20 hrs. G.M.T. and the minimum at 4 hrs. G.M.T. Over land, particularly in cities, we have superposed on this 'universal' variation, a local variation, apparently associated with local convection currents and variation in atmospheric pollution. Whipple and Scrase plotted a curve

showing the number of thunderstorms at different hours of G.M.T. over the earth as whole, and emphasised that this curve was very similar to the diurnal variation of the electric field. When the number of thunderstorms is maximum, the effect on the electric field is also maximum. Clearly the effect is conveyed at the same time all over the world on account of the high conductivity of the ionosphere.

How does thunderstorm generate charges? What sort of dynamo is a thunderstorm? For a long time much controversy has raged round this question. Simpson showed in 1909 that when drops of distilled water are broken in a vertical blast of air, the drops got positively charged, and the negative charge was given to the air. He propounded that this process was in operation in a thunderstorm on a large scale, and as a result the thundercloud got positively charged in the lower part and negatively charged in the upper part. This, however, did not agree with the potential gradient observed below and at some distance from the thundercloud. I showed in 1938 that rain water is not distilled water. The impurities are such that by breaking drops we can generate very little positive charge. When the impurities exceed a certain limit the drops may even become negatively charged.

In 1929, C.T.R. Wilson described in detail the process in which falling cloud particles could become charged in the presence of moving ions. The actual charge which the rain-drops acquire depends on the number of positive and negative ions, on their mobility and on the intensity of the electric field. In their work, Whipple and Chalmers show that in an atmosphere of ions, large or small, the maximum charge Q, which a drop of radius a cm. can acquire in a field of X e.s.u. is $-3Xa^2$ e.s.u. The process outlined by Wilson will make the lower part of the cloud negatively charged and the upper part positively charged. But observations show that drops can have charges greater than this maximum value. Therefore, they could not have acquired their charges merely by Wilson process.

A few years ago at the initiative of Simpson a large number of balloon soundings were made of thunderstorms by means of an instrument called alti-electrograph on which a trailing aerial or another which was directed upwards made marks according to the sign of the potential gradient. An analysis of the records indicated that the upper part of the cloud was positively charged and the lower part negatively charged, but in a certain number of active thunderstorms, there was a region at the base which was positively charged. In my own observations of thunderclouds which moved overhead, I found that the front part of the cloud was negatively charged, the central part at the base positively charged and the rear negatively charged.

In the method followed by me, there was no means of knowing the nature of charge in the top of the cloud, except by observing the form and pattern of lightning discharges. This would indicate a region of positive charge on the top but with an intermediate layer of negative charge between the positive charge at the base and the top positive charge.

The region of positive charge at the base where one would expect to get strong convection current is obviously a region where the Simpson process of generation of charge by breaking of drops is in operation. It is a mistake to imagine that any particular process would build up the distribution of intense charges in a thundercloud. Both the Simpson process and Wilson process must be in operation. Moreover thunderclounds usually extend considerably above the freezing level, and at that height cloud particles exist in the form of ice-particles. The collision of ice-particles makes them negatively charged, the positive charge being given to the air. These as they grow and sink down bring the negative charge to the lower parts of the cloud.

The majority of the lightning discharges occur between two parts of the cloud and only occasionally between the cloud and the ground. It has been observed that lightning discharge to ground almost invariably brings negative electricity. By means of Boys' rotating camera, Schonland has made intensive study of the manner in which lightning discharge takes place. Under the intense electric field, the negative ions slowly create a path from the cloud to the ground. This is the leader stroke. As soon as the path is created, there is the return stroke of positive charge from the ground into the cloud. The "leader" coming from the cloud develops a number of branches and eventually the main stem approaches the earth. Then a vigorous and much brighter luminosity travels rapidly up this stem, the branches lighting up in succession. Subsequent strokes are not branched, but they have the same double character, leader and return stroke. It has been shown by Schonland that these surges agree remarkably with the "wave-form" of atmospherics.

It has been estimated that a lightning flash will discharge about 20 coulombs of positive and negative electricity. There may be 10 or 15 lightning flashes in a minute and yet the charges are quickly regenerated. It is not easy to explain this quick speed of regeneration of charges in thunderclouds. A lightning discharge destroys charges only in small parts of the clouds, and the discharge itself must necessarily be associated with the creation of a large number of ions. Recent work also shows that ions are created in he process of condensation, evaporation and sublimation. In the intense

field of the thundercloud the ions are still ready to separate immediately after a lightning flash.

While occasionally we observe lighting to the ground we do not ordinarily observe lightning from the cloud to the ionosphere. Malan watched a cloud in South Africa at a distance of about 50 km. The base of the cloud was hidden by intervening hills and there were no bright flashes to blind his eyes to certain luminous discharges which went upwards from the cloud top. Most of the lightning in the storm was inside the cloud, but there were about a dozen of these disturbances through the upper atmosphere. More observations of this nature are required to definitely establish the part played by thunderclouds in the circulation of electricity.

When we measure charges on individual drops of rain we do not find that the successive drops during an interval of time are all positively charged or all negatively charged. There is always a mixture of positively charged and negatively charged drops. This has been observed by me in India and also by Chalmers in Europe. My observations showed that when the total rain collected in a period of 2 minutes was positively charged, this only meant that there was an excess of positively charged drops, and when it was negatively charged, there was an excess of negatively charged drops. The observed charges can be explained if the cloud particles which are charged colloidal particles coagulated to form rain drops.

Much work remains to be done on Atmospheric Electricity. In several parts of the world difficulties have been experienced in identifying the measured earth-air current with an expression of the kind $F(\lambda_+ + \lambda_-)$, where F represents the field strength and λ_+, λ_- the positive and negative conductivities. Many points require elucidation. We still do not understand precisely the role of the discharge from the innumerable sharp points on the surface of the earth and the space charge.

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THE F-TYPE RADIO-METEOROGRAPH AS AN INSTRUMENT TO MEASURE VERTICAL CURRENTS IN THE ATMOSPHERE

By S. P. Venkiteshwaran, B.A. (Hons.), F.A.Sc.

Received December 18, 1951

Summary

The paper describes the chief features of the fan used in the Indian F-type radio-meteorograph and how it enables one to know from the radiosonde data whether the balloon is descending due to accumulation of snow or strong vertical currents. Instances when the balloon went up and down due to accumulation and melting of snow have been described. The decrease in the rate of ascent and even the descent of the balloon due to strong downward currents in a thunderstorm on the 26th April 1950, have been estimated. The paper also shows how the F-type radiosonde data can be used to identify regions of clear air turbulence.

The F-type radio-meteorograph of the India Meteorological Department,[1] like the Vaisala or the British Meteorograph, employs a fan which rotates during the ascent of the balloon, but the design and mounting of the fan in the Indian instrument is very different from those in the others. The fan in the F-type meteorograph is made from a single sheet of paper; it is mounted in the instrument so as to rotate about a vertical axis when the balloon rises in the atmosphere (Fig. 1). In the Vaisala and British instruments, the fans are made of 3 or 4 cone cups mounted about a horizontal axis. In these instruments the cups can rotate both due to vertical ascent of the balloon and due to horizontal winds.

The chief feature of the fan in the F-type radio-meteorograph is that it rotates only when it moves relative to the air along the axis of rotation in the upward direction; horizontal winds at any level have very little effect. Moreover, during the ascent, the balloon moves horizontally with the speed of the wind and therefore the effect of the horizontal wind is unimportant.

As the fan in the F-type radio-meteorograph operates only during the upward motion along the axis of rotation, the rate of rotation of the fan serves as a very useful indication of the existence of vertical currents in the atmosphere. If the balloon develops a leak, the rate of ascent will first

decrease, and later the balloon will descend. This will be reflected in the rate of rotation of the fan, which will first begin to slow, and later stop when the balloon begins to descend. On the other hand, if snow accumulates on the balloon, the rate of rotation will decrease gradually and the rotation will stop as soon as the accumulation is sufficiently large to exceed the free lift of the balloon, and the balloon descends. However, in this case, when the balloon descends below the freezing level, the accumulated snow will melt and the balloon will rise again, and the fan will restart working. Dr. Suryanarayana and Mr. Kachare[2] had occasion to observe this phenomenon on two days (6th October 1950 and 7th October 1950) when F-type radiosonde ascents were made during rain. Fig. 2 shows the pressure

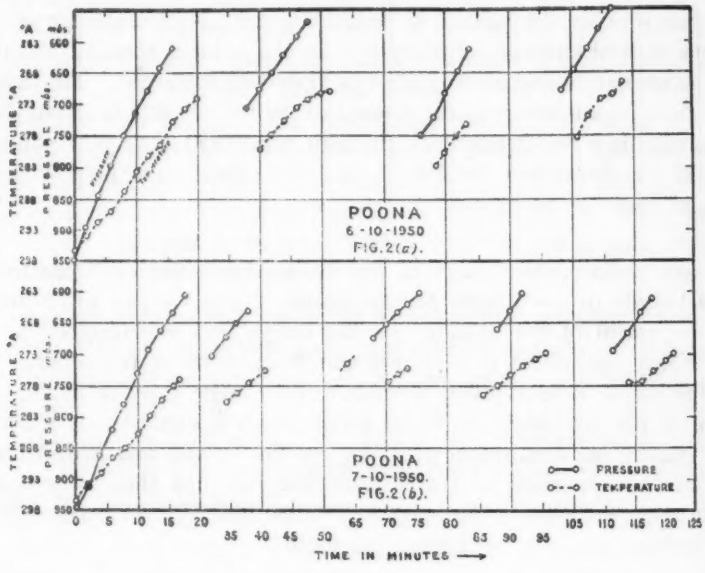

FIG. 2

and temperature distribution when the balloon went up and down due to the accumulation and melting of snow. It will be noticed that no signals were received every time the balloon descended due to the accumulation of snow, for, during this period, the fan was not rotating due to its motion in the reverse direction in the air.

In the case of all other types of radio-meteorographs, though one can observe the movement of the balloon up and down in the atmosphere from the pressure and temperature data, it cannot be said whether they are due

to vertical currents of air or due to accumulation of snow. In the case of the F-type radiosonde, however, if the balloon descends due to a strong downward current of air, the fan will be continuously rotating, and the rate of descent due to this downward current can be estimated from the rate of increase of pressure and temperature. Venkiteshwaran and Tilakan[3] had occasion to analyse the movement of a radiosonde balloon in a thunder cloud on the 26th April 1950. During this ascent, the balloon was once forced down due to strong downward currents and also later due to the accumulation of snow. However, these various stages could be distinguished and even the rate of descent of the vertical current estimated as described below.

Fig. 3 gives the variation of pressure and temperature with time experienced by the radiosonde; Fig. 4 gives the rate of rotation of the fan operating the radio-meteorograph. This rate of rotation is measured by the length of paper tape per complete Olland cycle and is given by the distance between two consecutive signals from the fixed reference contacts in

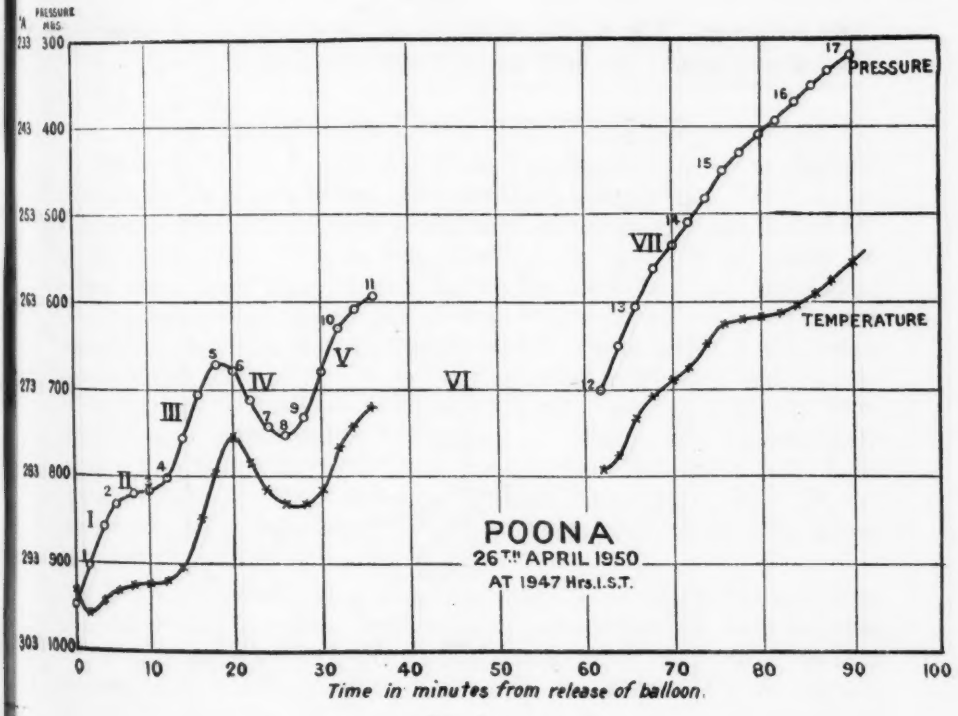

FIG. 3

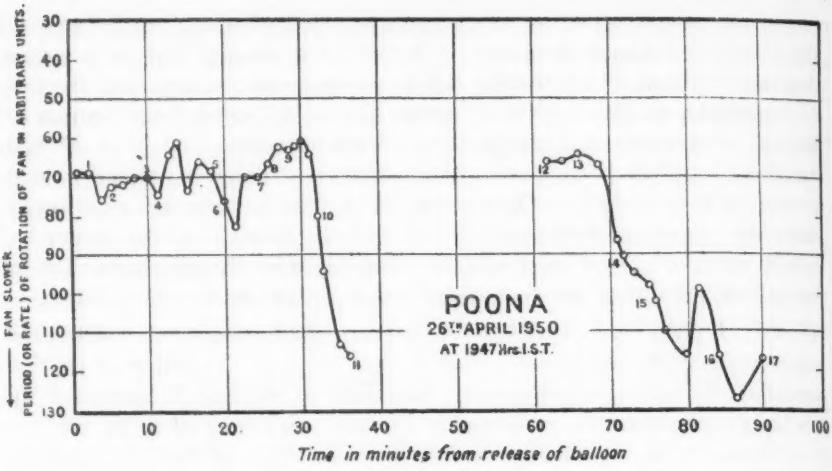

FIG. 4

the instrument. Fig. 5 gives the tephigram obtained from the ascent giving the distribution of dry bulb and wet bulb temperatures.

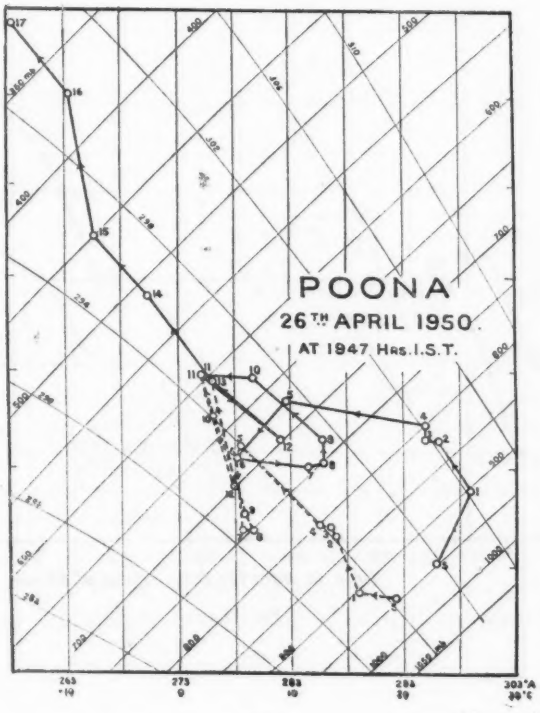

FIG. 5

It can be observed from Fig. 3 that in phase I, the balloon was rising uniformly for about 6 minutes till it reached the 827 mb. level when its rate of ascent was reduced for about 6 minutes. Later, it again rose uniformly for about 6 minutes more till it reached the 671 mb. level after which the balloon descended to the 750 mb. level in about 8 minutes. It again rose for about 10 minutes till it reached the 593 mb. level. After this no signals were received from the fan for about 24 minutes; later the signals were again received, but from a lower level, *viz.*, 700 mb. and continued thereafter till it reached 320 mb.

The approximate rates of ascent or descent of the balloon in the different phases are given below:

Phase	Characteristic points	Approximate rate of ascent (km.p.h)	Remarks
I	Upto 2	13	
II	2—4	3	
III	4—5	15	
IV	5—8	—7	Balloon descending; rate of descent about 11 m. p. h. between points 6 and 7
V	8—11	11	Rate of ascent about 18 m.p.h. between 9 and 10
VI	11—12	..	Balloon descended due to accumulation of snow
VII	12—17	13	

When the ascent curves in Figs. 3 and 4 are examined, it will be observed that during the phases II and IV, though the balloon was rising at an appreciably lower rate in phase II and even descending in phase IV, the fan in the meteorograph was rotating almost at the same rate as during the period immediately after release. As the fan can rotate only when there is an opposing wind, the balloon must have experienced strong downward currents in these two phases. Comparing the rate of ascent in the region corresponding to phase I with that at phase II, it is observed that the rate of ascent had decreased from about 13 km.p.h. to about 3 km.p.h. from which it can be inferred that the downward current was approximately 10 km.p.h. in phase II. Similarly, a rate of ascent of about 15 km.p.h. in phase III became a rate of descent of about 7 km.p.h. in phase IV, the maximum downward current experienced by the balloon then being not less than 22 km.p.h.

In phase VI, the balloon was descending and as the fan was not rotating, the descent must have been due to thick icing on the balloon. That this is so is confirmed by the fact that the temperature of the air at the level corresponding to the beginning of phase VI was about 2° C. As the rate of ascent began decreasing even from the 630 mb. level, it is possible that

the snow had started falling and accumulating on the balloon even from this level.

When the balloon descended, the ice should have melted and therefore the balloon began rising again as shown in phase VII. But the rate of ascent now was only 8 km.p.h., and this is probably because the balloon started rising before all the snow collected on it had melted, and even reached the freezing level again when further melting would not have been possible.

From the tephigram in Fig. 5 it will be observed that there was a ground inversion due to the rain cooled air. When the balloon reached the 671 mb. level, the dry bulb fell suddenly to that of the wet bulb indicating a very high super-adiabatic lapse rate. Simultaneously, the balloon was caught in the downward current which brought it down from the 671 mb. level to the 750 mb. level. During this descent, the rise of temperature was almost along the dry adiabatic.

Till the balloon reached the 671 mb. level after its release, the wet bulb temperature was changing along the saturation adiabatic. But during the descent of the balloon, though the dry bulb temperature changed along the dry adiabatic, the wet bulb temperature remained almost the same. The reduction in the wet bulb potential temperature is presumably due to the descending column entraining air from outside the cloud.

The details of the various phases have been described already in the previous paragraphs. It is, however, interesting to note that during the last phase VII, the lapse rate was almost equal to that of the saturation adiabatic upto about 450 mb. above which it decreased to about 1° C./km. till 372 mb., above which the lapse rate again increased. Probably, the anvil of the thunderstorm was in the region between 450 and 372 mb. *i.e.*, between 6·8 and 8·3 km. above sea-level.

It may also be mentioned in this connection that even in clear weather, the variations in the rate of rotation of the paper-fan are yielding valuable information about regions of turbulence in the atmosphere, whose existence cannot be known at present except from aircraft reports.[4] As the rate of rotation of the fan seems to indicate the vertical forces acting on it, it was decided to test whether the fluctuations in the rate of rotation of the fan are true indications of certain characteristic features in the atmosphere, and if so, to what extent. Fig. 6 shows the rate of rotation of the fans in two instruments let off simultaneously at Poona with two independent balloons. If the changes in the rate of rotation of the fan represents a characteristic property of the air mass, it should be indicated from two simultaneous ascents

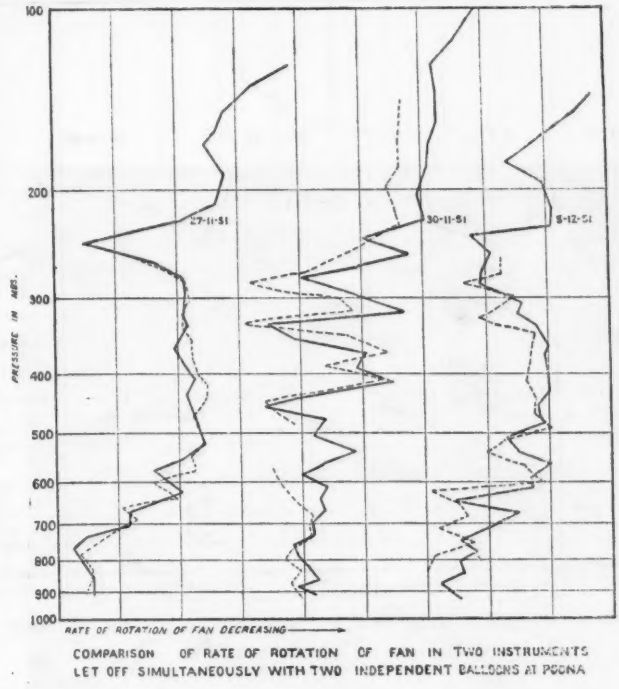

FIG. 6

from different places. Fig. 7 shows the variation in the rate of rotation of the fan at Poona (18° 32′ N and 73° 51′ E) and Nagpur (21° 09′ N and 79° 07′ E). The ascents show a degree of agreement which confirms the view that the rate of rotation of the fan represents some specific property of the air mass. Fig. 8 shows a series of curves showing the variation of the rate of rotation of the fan at various levels over Poona from the 11th March 1951 to the 14th March 1951. It will be observed from these that in the region between 400 mb. and 300 mb. there were frequent and large increases in the rate of rotation of the fan. Its occurrence in a particular region, its persistence on a few days and absence later, are significant.

An increase in the rate of rotation of the fan can either be due to an increase in the rate of ascent of the balloon relative to the surrounding air or due to a downward current of air. These rapid increases or decreases in the rate of rotation of the fan can be attributed only to strong downward or upward currents due to turbulence occurring in these regions. As the

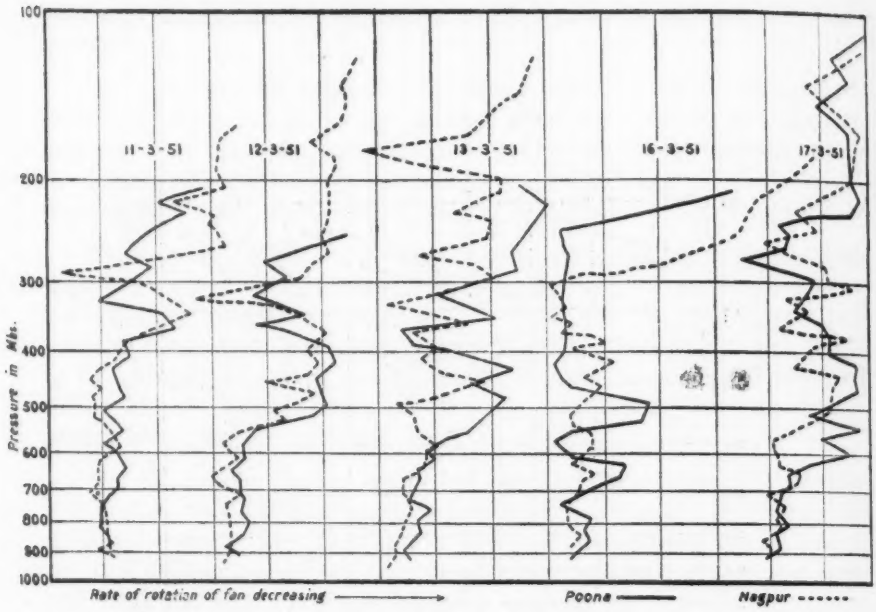

FIG. 7. Comparison of Rate of Rotation of Fan in Radiosondes Released at about 1500 hrs. G.M.T. at Poona and Nagpur.

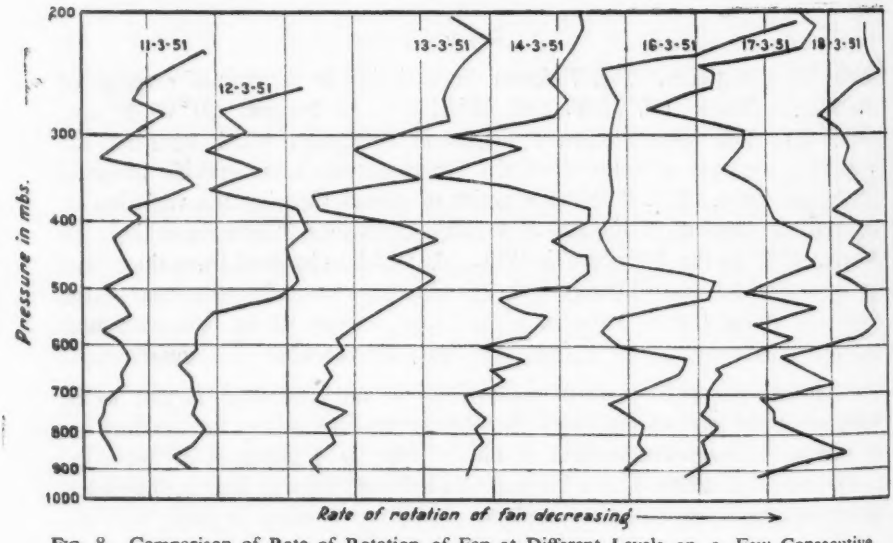

FIG. 8. Comparison of Rate of Rotation of Fan at Different Levels on a Few Consecutive days at Poona.

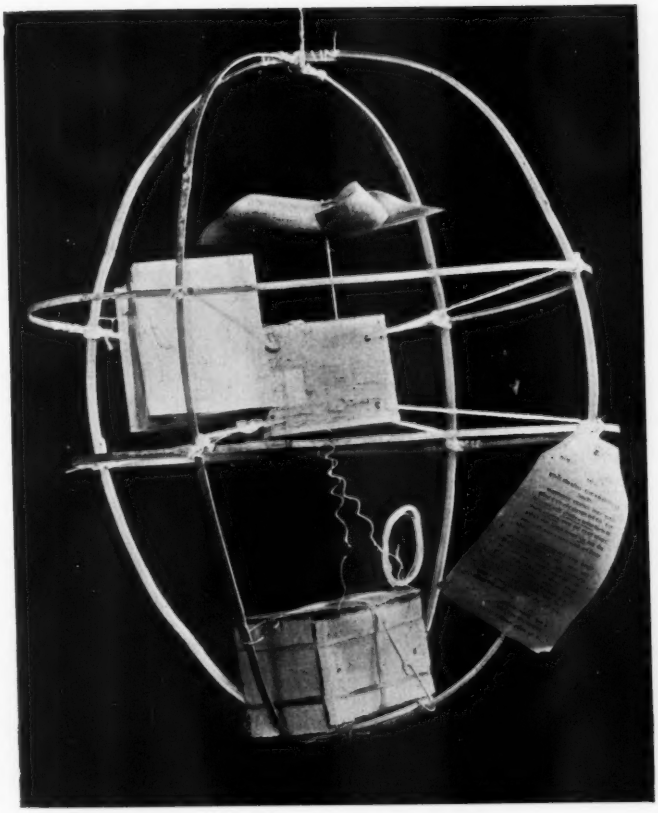

FIG. 1

variations in the rate of rotation of the fan are of short durations and represent the effect of turbulence, they cannot be observed from the rate of ascent of the balloon computed from the observations of pressure signals received from the radio-meteorograph, nor by any of the methods of observations now available. With the increase in the frequency of high level flying, the phenomenon of clear air bumpiness has come to light. It appears from the above analysis of the F-type radiosonde records, that this simple instrument can be a tool for locating regions of turbulence at any height in the atmosphere. With standardised fans, it may be possible not only to locate such regions, but to compare the intensity of the turbulence from day to day. The F-type has certain unique features not available with any other type of radiosonde.

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MEASUREMENTS OF ATMOSPHERIC OZONE AND ITS VERTICAL DISTRIBUTION AT KODAIKANAL (LAT. 10° 14′ N)

By Dr. R. V. Karandikar, M.Sc., Ph.D.

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(Communicated by Dr. K. R. Ramanathan, F.A.Sc.)

Abstract

Using a Dobson-type photoelectric ozone spectrophotometer, measurements of the total ozone amount and its vertical distribution in the atmosphere were made at the Solar Physics Observatory, Kodaikanal (Lat. 10° 14′ N) for a few months in 1948–49. The daily values of ozone showed little variation with other meteorological factors. Umkehr curves corresponding to total ozone amounts 0·175 cm. and 0·184 cm. were used to calculate the vertical distributions and these gave 29·1 km. and 28·8 km. as the average heights of atmospheric ozone over Kodaikanal.

From a review of the previous work on the height distribution of atmospheric ozone in different latitudes, it appears that the average height of ozone over Kodaikanal is the highest obtained so far. The general trend of variation of average heights of ozone in different latitudes is that, while in middle latitudes the height decreases rapidly with increasing latitudes, in low and high latitudes this rate becomes smaller, giving a maximum height of about 30 km. near the equator and a height of about 20 km. somewhere in the polar regions.

1. Introduction

In two previous papers,[1,2] measurements of the total amount of atmospheric ozone and its vertical distribution made with a Dobson-type photoelectric spectrophotometer at the latitudes of Delhi (28° 35′ N) and Poona (18° 31′ N) were described. The analysis of the data gave the annual variation of ozone at these places more or less similar to that obtained by others at some places in the tropics. There were marked variations in the day-to-day values during the period of western disturbances; but in the monsoon season the values were practically steady, with no marked variations with changes in weather. The average heights of ozone were found to range from 26·3 to 25·1 km. for 0·155 to 0·217 cm. of ozone over Delhi and about 28·0 km. for 0·170 cm. of ozone over Poona. These heights for the two low-latitude

places were seen to be greater than those obtained by Dobson and others for corresponding quantitites of ozone at Arosa[3] and Tromso[4] in the middle and high latitudes. Similar information for places in very low latitudes was however still very meagre. A series of observations of the total amount of ozone at Kodaikanal (Lat. 10° 14′ N) was made with the old photographic instrument in 1928–29 under Dobson's first world-wide ozone survey.[5] A knowledge of the vertical distribution of ozone over this place was, however, still lacking and the need was therefore expressed for the continuation of observations with the new photoelectric instrument at this latitude, which might yield interesting and fruitful results.

Recently such observations were carried out at the Solar Physics Observatory, Kodaikanal, for some months in the monsoon season in 1948 and later in the early hot season in 1949 with the same instrument as was used at Delhi, Simla and Poona. Apart from the day-to-day values of total ozone from direct sun observations, Umkehr curves were obtained on some clear days from observations of the light scattered from the blue zenith sky. The present paper gives the results of analysis of these observations. The mean curve corresponding to an ozone amount 0·175 cm. gave 29·1 km. as the height of ozone over Kodaikanal; another single-day curve corresponding to 0·184 cm. of ozone gave 28·8 km. as the average height. From a review of the previous work on height distributions of atmospheric ozone at different places, it appears that the average height of ozone over Kodaikanal situated near the equator is the highest obtained so far as compared to that at any other place of higher latitude. Also the general trend of the variation of average height of atmospheric ozone in different latitudes suggests that, while in the region of middle latitudes there is a rapid decrease in the height with an increase in the latitude, the rate of change becomes smaller in the low and high latitudes and the curve might give a maximum height of about 30 km. near the equator and a height of about 20 km. somewhere in the polar regions.

2. Observational Data

Details regarding the general principles of the method of observation, reduction of observational data and the calculation of results have already been given in previous papers, and particulars regarding the new work only will be given here. It may be mentioned that owing to the frequently poor sky conditions at Kodaikanal during the period of observations and also to long breaks in the observations due to other engagements, the observational data at Kodaikanal are not so extensive as that obtained at other stations in India. Though the work was begun in August 1948, due to

both S.W. and N.E. monsoons, clear blue sky was not available for observations for a long period. During the monsoon season, day-to-day values of ozone from direct sun observations only could be obtained. Some worthwhile zenith sky observations were obtained later in the month of March 1949. Moreover, the climatic conditions at Kodaikanal were such that the afternoons there were generally cloudy and continuous observational work could be done only in the mornings. The Observatory is situated at a height of about 2·34 km. above mean sea-level; the quality of the sky was, however, frequently poor and scattering due to dust and haze in the atmosphere was not negligible.

(*A*) *Total ozone amount.*—Direct sun observations were carried out whenever clear sunshine was available and total ozone values were calculated from these using the generalized formula suggested in a pervious paper.[6] The calibration of the optical wedges and other constants of the instrument were occasionally checked. Observations to study the diurnal variation of ozone were taken on some especially clear days and the curves showed a general trend similar to that obtained at Delhi, *viz.*, afternoon values generally higher than the morning ones, with a dip near about the local noon. The results are, however, not quite decisive and this point requires further critical study. Table I gives the daily values of ozone (averages of morning observations only) for the different months in which observations were carried out. The monthly means are given at the end of each column and the means for the same months from observations made in 1928–29 are also given for comparison. It appears that the values obtained in 1928–29 are, for some reason, higher than those obtained in the present series. The present values obtained with the photoelectric instrument (No. 10) are, however, directly comparable with those obtained at other places in India and seem to be more reliable also.

Plotting the daily ozone values against the pressure at 0800 hrs., minimum temperature, rainfall, etc., at Kodaikanal showed no correlation between them. In the monsoon season, the average ozone amount was low and the day-to-day fluctuations were also small, the monsoon thus showing to have a sort of stabilizing effect on the total ozone amount. In the early hot season, the values had started going up, but unfortunately the observations could not be continued. The fact that the ozone amount is more or less insensitive to surface conditions in all these months suggests that tropical ozone lies mostly high up in the atmosphere in a region little disturbed by surface weather changes.

TABLE I

Daily values of atmospheric ozone at Kodaikanal (Lat. 10° 14′ N) in cm. at N.T.P.

Date	August 1948	September 1948	October 1948	March 1949
1	..	0·172	0·169	0·163
2	..	0·162	0·167	0·160
3	..	0·171	overcast	0·165
4	..	0·173	0·165	0·173
5	..	0·173	0·171	0·164
6	..	0·173	0·171	0·170
7	..	overcast	0·176	0·172
8	..	0·172	0·177	0·172
9	..	0·171	0·172	0·175
10	..	0·173	0·172	0·175
11	..	0·167	0·174	0·178
12	..	0·169	0·175	0·177
13	..	0·170	overcast	0·181
14	..	0·170	,,	..
15	0·173	overcast	,,	0·185
16	0·173	0·168	,,	0·184
17	0·177	0·170	,,	
18	0·174	overcast	,,	
19	0·174	0·163	,,	
20	0·174	0·174	,,	
21	0·172	overcast	,,	
22	0·173	0·171	,,	
23	0·173	0·172	0·170	
24	0·162	0·169	0·170	
25	overcast	0·177	0·173	
26	0·175	0·180	0·166	
27	overcast	0·176	overcast	
28	0·174	0·173	0·165	
29	0·173	0·174	0·164	
30	0·171	0·178	..	
31	0·174	..	..	
Monthly means 1948–49	0·173	0·172	0·170	0·173
Monthly means 1928–29	0·205	0·206	0·203	0·199

(*B*) *Zenith sky observations.*—On days when the quality of the sky was fairly good and steady, complete series of the observations on the light scattered from the clear blue zenith sky were taken. But the amounts of ozone on all such days varied between 0·172 and 0·184 cm. only. Fig. 1 gives the observational data in the form of plots of Log I/I′ against Z^4, where I and I′ are the intensities of the zenith-scattered light of wavelengths 3110 Å

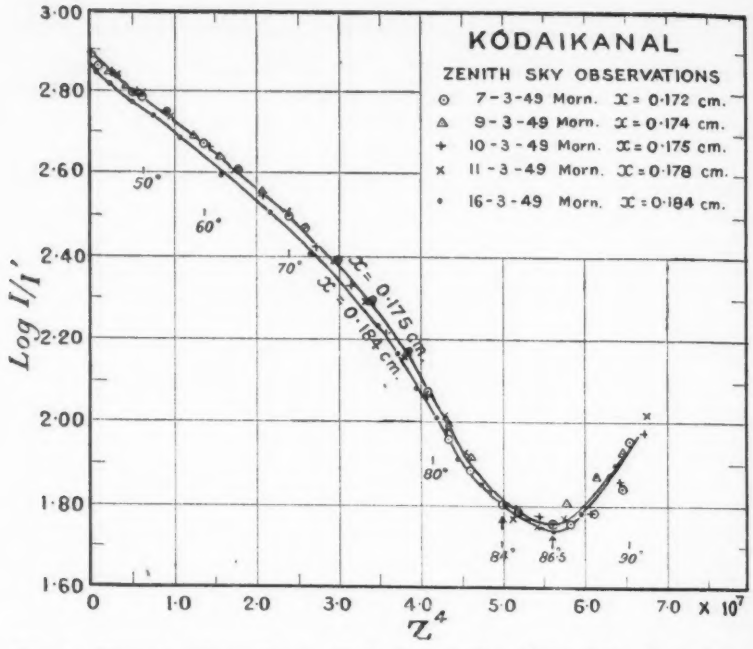

FIG. 1. Observed values of Log I/I′ in the zenith-scattered light for various zenith angles Z of the sun and with different ozone amounts x at Kodaikanal.

and 3300 A reaching the instrument and Z is the zenith distance of the sun. The diagram gives two Umkehr curves corresponding to ozone amounts 0·175 cm. and 0·184 cm. The first is the mean curve through observational points obtained on four different days with ozone amounts varying between 0·172 and 0·178 cm.; the other is a single-day curve with ozone amount 0·184 cm. The scatter of observational points for large zenith distances of the sum is such that it is thought advisable to make the two curves merge together near $Z = 90°$.

3. CALCULATION OF THE HEIGHT DISTRIBUTION AND RESULTS

Table II gives the values of Log I/I′ for the two observational curves corresponding to different zenith distances Z of the sun. As in the previous work, method B was used and calculations were carried out assuming different ozone amounts in the different sections of the atmosphere and adjusting them by trial and error until satisfactory agreement was reached between the observed and calculated values of Log I/I′. To eliminate the instrumental constant C, $Z = 50°$ was chosen as the angle for which the observed and

TABLE II. *Observed values of Log I/I′ at Kodaikanal for different values of Z*

Z	$Z^4 \times 10^{-7}$	Log I/I′ Total ozone content in cm. at N.T.P.	
		0·175	0·184
50°	0·625	2·785	2·754
60°·75	1·36	2·674	2·645
70°	2·40	2·498	2·465
80°	4·10	2·065	2·033
84°	4·98	1·816	1·807
86°·5	5·60	1·752	1·738
90°	6·56	1·940	1·940

calculated curves should be made to coincide, and the distribution of ozone was adjusted to secure agreement at higher values of Z. Since the height of Kodaikanal is 2·34 km. above sea-level, the layer of the atmosphere between sea-level and 2·34 km. (*i.e.*, up to the average pressure level 773 mb. corresponding to the period of observations) does not take part in the scattering or absorption processes, and the calculations were modified accordingly. Table III gives the amounts of ozone in cm. per km. height in the different sections obtained from the final calculated distributions.

TABLE III. *Amounts of ozone in cm. per km. height in different layers of the atmosphere over Kodaikanal*

Layer No.	Boundaries of layer in km.	Total ozone content in cm. at N.T.P.	
		0·175	0·184
6	45—54	0·0002	0·0002
5	36—45	0·0017	0·0017
4	27—36	0·0110	0·0110
3	18—27	0·0059	0·0069
2	9—18	0·0005	0·0005
1	2·34—9	0·0002	0·0002
Average height of C. G. of ozone above sea-level in km.		29·1	28·8

The concentration of ozone in the surface layer is shown to be 0·0002 cm. of ozone per km. height and this is likely to suggest that the surface concentration at Kodaikanal (and also at Poona given in the previous paper[2]) is too low as compared with that in higher latitudes (*e.g.*, for Arosa and Tromso, it is stated to be of the order of 0·004 cm. per km. height). Actually nothing is known, since no independent experimental data regarding surface concentration of atmospheric ozone in India are available. Whatever concentrations for the different layers were assumed in the trial and error process to get a good fit between the calculated and observed Umkehr curves are presented. After allotting necessary ozone amounts to the higher layers, whatever is left is allocated to the surface layer. In this procedure, it was found that the higher layers required so much ozone-loading for a good fit that very little ozone was left for the surface layer and hence a nominal quantity 0·0002 cm. per km. was allotted to it.

Uniform distribution of ozone is assumed within each layer; hence the centre of gravity of each layer is at its midpoint and the centre of gravity of the total atmospheric ozone can be found easily by taking moments about the earth's surface; these are given at the bottom of Table III.

Fig. 2 gives both the block diagrams and smooth curves of the vertical distributions of ozone over Kodaikanal. For comparison, the vertical

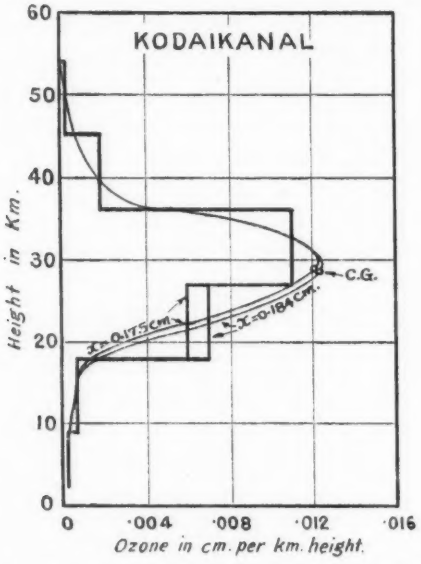

FIG. 2. Calculated vertical distributions of ozone over Kodaikanal corresponding to different total ozone amounts x.

distribution curves obtained at Kodaikanal and other places in India and Europe are shown together in Fig. 3. It may be noted that each distribution

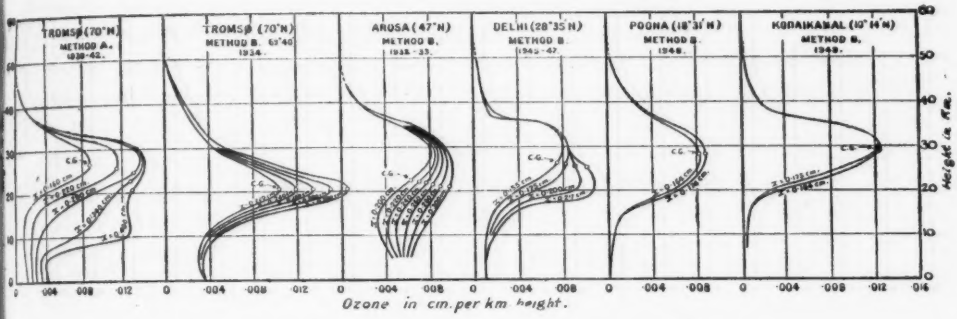
TROMSØ (70°N) METHOD A. 1939-42.
TROMSØ (70°N) METHOD B. 1934.
AROSA (47°N) METHOD B. 1932-33.
DELHI (28°35'N) METHOD B. 1942-47.
POONA (18°31'N) METHOD B. 1948.
KODAIKANAL (10°14'N) METHOD B. 1949.
Ozone in cm. per km height.
Height in Km.

FIG. 3. Height distributions of atmospheric ozone in different latitudes.

curve for Kodaikanal has a single pronounced maximum near about 30 km. most of the ozone lying between 20 and 40 km. These curves may be compared to the distribution curves at Delhi and Tromso (Method A) which show more interesting features. The ratio of ozone to air by volume at different levels in the atmosphere was also calculated and the results are summarised in Table IV.

TABLE IV. *Height distribution of atmospheric ozone over Kodaikanal as cm. of ozone per km. height and as ratio* R *of ozone to air by volume*

Height above M. S. L. in km.	Total ozone in cm. at N.T.P.			
	0·175		0·184	
	O_3/km. $\times 10^3$	$R \times 10^6$	O_3/km. $\times 10^3$	$R \times 10^6$
50	0·15	1·9	0·15	1·9
45	0·65	4·2	0·65	4·2
40	1·60	5·1	1·60	5·1
35	8·30	11·7	8·30	11·7
30	12·35	8·12	12·55	8·25
25	9·10	2·61	10·10	2·89
20	3·05	0·38	3·90	0·49
15	0·60	0·032	0·60	0·032
10	0·25	0·007	0·25	0·007
5	0·20	0·003	0·20	0·003
2·34	0·20	0·003	0·20	0·003

4. DISCUSSION OF RESULTS

Table V summarises the information available so far regarding the average heights of atmospheric ozone in different latitudes. Measurements made with the Dobson-type of instrument and using Method B for calculation are given first. Results for an ozone value equal to 0·175 cm. where available and interpolated or extrapolated results in other cases are indicated.

TABLE V

Average heights of atmospheric ozone in different latitudes

Author	Year	Place	Latitude N	Method	Total ozone in cm. at N.T.P.	Average height in km.
Karandikar ..	1949	Kodaikanal	10° 14′	Umkehr effect (B)	0·175	29·1
Karandikar and Ramanathan	1948	Poona	18° 31′	do	0·174	28·0
do ..	1945–47	Delhi	28° 35′	do	0·175	25·9
Götz, Meetham and Dobson	1932–33	Arosa	47°	do	0·180 (extrapol.)	22·6
Meetham and Dobson	1934	Tromso	69° 40′	do	0·220 & all other values	20·8
Tonsberg and Langlo	1939–42	Tromso	69° 40′	(A)	0·175 (interpol.)	26·5
Strong and Watnabe	1940	Palomar Mtn.	33° 22′	Residual ray apparatus	0·234	22·2
Regener and Regener	1934	Stuttgart	48° 47′	Sounding balloon	0·270	22
O'Brien, Mohler and Stewart	1935	Black-hills, South Dakota	44°	Explorer II	0·190	28
Coblentz and Stair	1938	Beltsville, Maryland	39°	Photocell filter and radio transmitter in balloon	0·20 to 0·21	22
Naval Res. Lab., U.S.A.	1946 and 1948	White Sands, New Mexico	33°	V-2 rocket	0·238 0·20	22·6 20·5

It will be seen that the average height of ozone over Kodaikanal is the highest obtained so far as compared to that at any other place of higher latitude. The same results are shown graphically in Fig. 4, giving the variation of the average height with the latitude of the place. On joining the points corresponding to Method B of calculation, the curve obtained is remarkably smooth. It shows a rapid decrease of the average height with increasing latitudes in the region of middle latitudes, but towards the pole and the equator this rate becomes smaller. For Tromso (Lat. 70° N), in addition to the short-term series of observations obtained by Meetham and Dobson in 1934, there is the other long-term series obtained by Tonsberg and

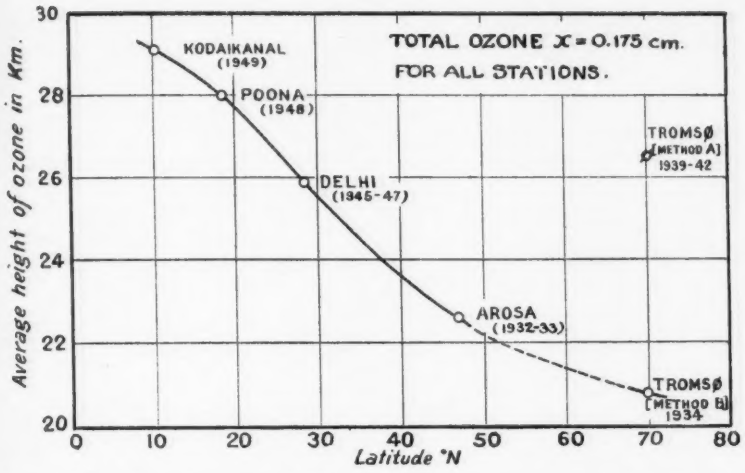

FIG. 4. Variation of average height of atmospheric ozone with latitude.

Langlo[7] during 1939–42 using Dobson's method A for calculation. The point corresponding to this series obtained by interpolation, however, lies far out from the above curve. Considering the large day-to-day and seasonal variations of the total ozone in these high latitudes, similar large fluctuations in the ozone distribution and also its average height are naturally expected and hence it is not surprising if the results obtained in different seasons separated by many years and also deduced by two different methods show such differences. It is again interesting to note that according to the present knowledge about the latitudinal variation of total ozone, at least in the northern hemisphere and almost throughout the year, the total ozone increases from the equator towards the higher latitudes, giving a maximum near about 60°–65° N and then decreases towards the pole.[8] It is quite likely that the average height of ozone might also show some interesting features in the neighbourhood of these latitudes. At present, no observations of the average height of ozone are available for latitudes beyond 70° N and hence the nature of the curve in this region is rather uncertain. From the general trend of the curve, however, it appears that the average height might have a maximum value of about 30 km. near the equator and a value of about 20 km. somewhere in the polar regions. The possibility of the heights increasing again beyond 60°–65° N towards the pole is also not ruled out.

A new method of measuring the mean height of the ozone in the atmosphere has been developed by Strong[9] and Watnabe.[10] They measured the

total amount of ozone from the absorption of the solar radiation in the Hartley band and in addition measured the absorption in the 9·6 μ ozone band by means of a residual ray apparatus. The absorption in the infra-red band was shown to vary as the fourth root of the total pressure under which the ozone exists, and hence the pressure at the average height of the ozone layer, and thus its height was calculated. The method is quick and an estimate of the average height can be obtained every half an hour so that changes in the level of ozone can be followed during a day. The method, however, does not give any information about the vertical distribution of ozone. Their measurements at Palomar Mountain (Lat. 33° 22′ N, Alt. 5,600 ft.) during June, July and August, 1940, gave a mean height of 22·2 km. corresponding to a mean ozone value 0·234 cm. and this is indicated in Table V for comparison. The individual heights varied between 20·4 and 24·7 km. corresponding to 0·271 and 0·215 cm. of total ozone.

Besides the observations of the above type, there are a few reliable vertical distributions of ozone obtained by other direct methods and these are also indicated in Table V. E. and V. H. Regener[11,12] obtained photographs of the solar spectrum by sending a quartz spectrograph in a sounding balloon at Stuttgart in Germany and determined the amount of ozone above the balloon at different heights, thus giving the vertical distribution of ozone. The earlier flight in 1934 extending up to about 31 km. showed considerable ozone in the troposphere, but the later two flights in 1937 extending only up to 15 km. showed very much less ozone in the troposphere. From the curve of the 1934 flight, an estimate of the average height of ozone was obtained by assuming a distribution for the residual 0·06 cm. of ozone above 30 km. similar to that obtained by Götz and others[3] at Arosa.

Recently, V. H. Regener[12a] has published a preliminary report of his measurements of the vertical distribution of ozone over New Mexico (Lat. 35° N) from four sounding balloon flights made in 1950 upto about 30–32 km. using a small light-weight quartz spectrograph and photographic photometry. His curves exhibit more detail, show somewhat lower positions of maxima and indicate higher concentrations of ozone at low altitudes. The total ozone values (0·33 to 0·40 cm.) are unusually high for the latitude of New Mexico. No immediate relationship between the upper winds and ozone distribution was apparent.

A similar method was used by O'Brien and others[13] in the Stratosphere Flight of Explorer II on November 11, 1935, to get the vertical distribution of ozone. The values up to 22 km. were obtained from the sun spectra and

the values further up were estimated from the sky spectra. The average height calculated from their published curves is given in Table V.

Coblentz and Stair[14] have used unmanned balloons to carry aloft a photocell, a filter-radiometer and transmitter to record the ultraviolet intensities of solar radiation up to heights of 23 to 27 km. and thereby determined the distribution of ozone in the stratosphere.

More recently, solar spectra photographed in the V-2 rocket flights[15,16] over White Sands, New Mexico, have provided ozone data to the greatest altitudes. Results from two rocket flights made in 1946 and 1948 have been published and these give height distribution curves of ozone up to about 67 km., more or less in agreement with previous distributions.

The information regarding the vertical distribution of atmospheric ozone listed so far is too meagre, being limited to a very small portion of the earth's surface, and no definite conclusions can be drawn as regards the real nature of the height of the ozonosphere in different latitudes until more numerous observations at widely scattered stations over the globe are available. The question is, however, more complicated as it is likely that in the lower stratosphere and also in the troposphere, ozone might tend to accumulate in certain layers depending upon the stability of stratification as a result of photochemical and other processes at work in the atmosphere, and large fluctuations in the vertical distribution of ozone are quite possible. It is therefore rather doubtful how far the average height of ozone over a place has any practical significance. An attempt is only made here to collect the available information and give a rough idea of the picture as it stands at present.

5. Acknowledgements

The observations recorded in the present paper were made with the Dobson spectrophotometer belonging to the India Meteorological Department and the author's thanks are due to the Director-General of Observatories for the use of the instrument and to Dr. A. K. Das, Director, and other staff of the Kodaikanal Observatory, for giving all necessary facilities for the observational work at Kodaikanal. Thanks are also due to the Board of Scientific and Industrial Research for the award of a Research Fellowship during the period of work. The author wishes to express his grateful thanks to Professor K. R. Ramanathan for his interest and advice throughout the present work.

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THE GENESIS AND MOVEMENT OF THE NOR'WESTERS OF BENGAL*

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The Nor'westers of Bengal† are thunderstorms with which violent squalls are associated. First seen, perhaps on an isolated day in the month of February in association with a western disturbance, it becomes a familiar feature of the hot afternoons of April and May. Thereafter with the onset of monsoon, their frequency and violence decrease considerably. The down-draft from the thunderstorms which constitutes the squall frequently strikes from the northwest, which has given the Nor'wester its popular name. However, a good many of the squalls strike from other directions also. Other well-known features of a thunderstorm, *viz.*, thunder, lightning, rainfall, drop in temperature, rise in humidity and rise in pressure, are common to Nor'westers also. The Nor'wester is shortlived. Starting on most days with almost clear skies in the hot and uncomfortable afternoon, the approach, development and the fury are practically over in an hour or two leaving fine and cool weather behind.

These thunderstorms seem to develop anywhere over Bengal and the adjoining areas in the Nor'wester season. But investigations[15] have shown that there are a number of susceptible spots over the hilly regions or the base of the hills where some of the earliest thunderstorms form and then the activity seems to move in some direction. These 'soft' spots and the directions of movement are illustrated in Fig. 1.

It is generally believed[5] that these thunderstorms are caused by the interaction of the main air masses of the season, *viz.*, a moist S.E./S.W. air in the lower layers, with a dry W.-N.W. air, over it as in the sectional diagram given in Fig. 2. The thermodynamical character of the air masses reveals

* Abridged from a report presented in the Symposium on "Physics of Thunderstorms," under the auspices of the Indian Academy of Sciences in New Delhi on the 28th December, 1951.

† Locally known as "Kal-Baishakhi" or the calamities of the month of "Baishakh" which covers the period mid-April to mid-May, when the destructive violence of the squalls is felt and feared most by the people.

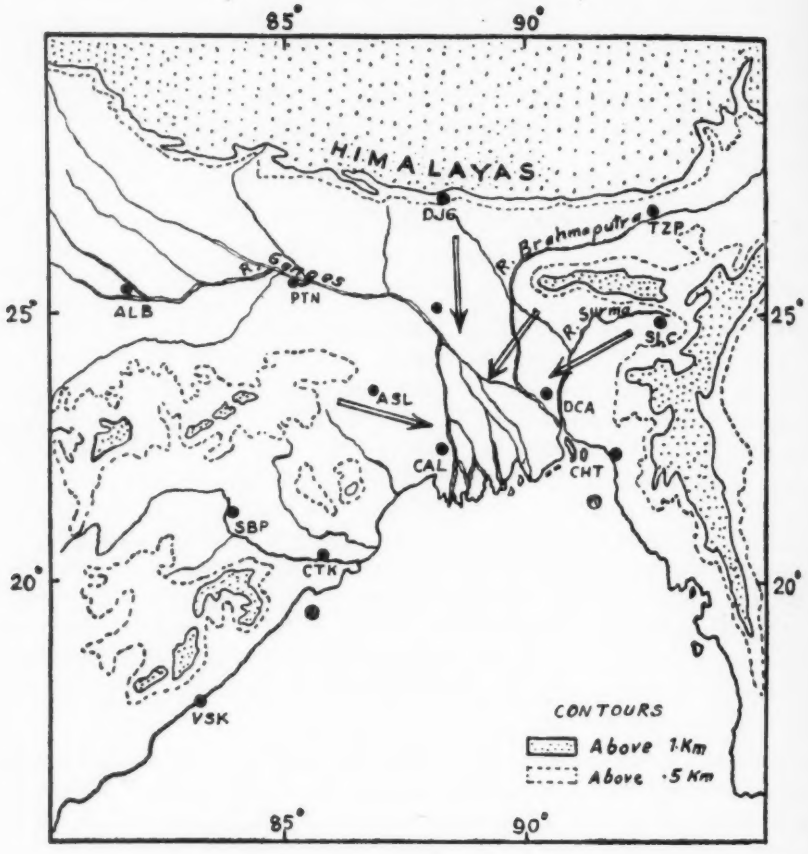

FIG. 1

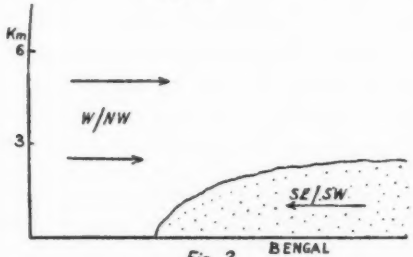

Fig. 2.

the presence of considerable amount of energy of latent instability,[6, 12] even after allowing for entrainment of air from the environment, and this energy

when released, manifests itself as a thunderstorm.[6] For the release of energy of latent instability, however, it is essential to bring about a condition which induces the ascent of air either from the surface or from some level higher up. A process which functions as above is known as 'Trigger Action'. Some of the well-known triggering processes which may operate individually or jointly are discussed below.

(*a*) Insolation,[6] well known for causing the heat thunderstorms during the afternoon (Fig. 3). The differentia! effect of insolation over rocky areas

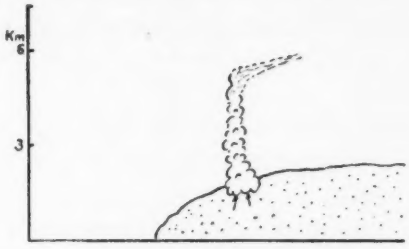

Fig. 3.

as compared with plains, makes it more intense over the Chota Nagpur hills and the base of the hills to the north and east, with the result some of the earliest thunderstorms form there. The effect of anabatic winds of the hill sides in the development of these thunderstorms in the afternoon is also similar.

(*b*) Cold front associated with a western disturbance travelling from west to east through Bengal, may cause Nor'westers at any time during the day and night by frontal action (Fig. 4). The katabatic flow[10, 11] from the base of Himalayas to the north, base of the Khasi hills and the flow through the Surma Valley also acts like a cold front (Fig. 5) the action of which is mainly confined to the night and earlier part of the morning.

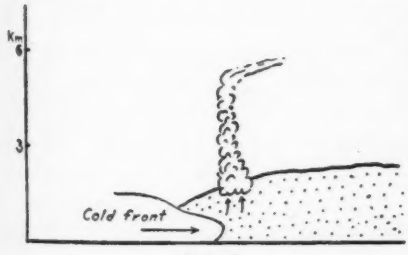

Fig. 4.

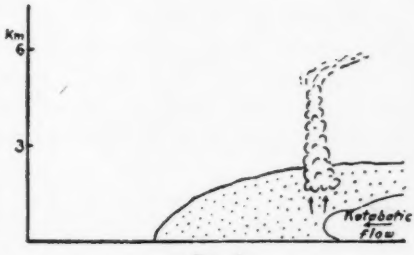

Fig. 5.

(*c*) Action of cold outflow from another thunderstorm in the neighbourhood operate as follows:

(i) *From the surface layers*[2, 3].—The mass of cold air left by a downdraft is cold and deep enough (upto 2,000-3,000 ft.) to act like a miniature cold front in inducing more thunderstorms (Fig. 6).

(ii) *From the upper layers*[12].—As pointed out by the author in 1948, a thunderstorm in the dissipating stages brings about a considerable fall in temperature at the upper levels also. This mass of cold air, in the process of being carried downwind and lowering the upper air temperatures in the vicinity increases instability and generates more thunderstorms (Fig. 7).

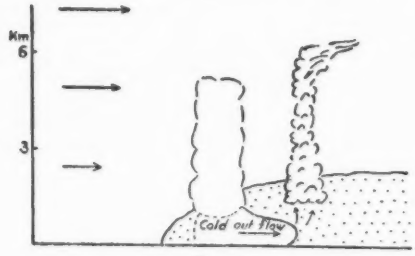

Fig. 6.

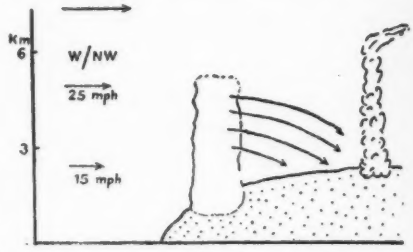

Fig. 7.

This aspect was studied further with the aid of a few special radio-sonde ascents in May 1951 in Calcutta. The changes in temperature during the progress of the Nor'wester and afterwards, are clearly brought out by the tephigrams for a typical day reproduced in Figs. 8, 9 and 10. When the thunderstorm was in progress (mature stage), there was a fall in temperature at 600 mb. level with no sign of cold pool on the ground. But after the

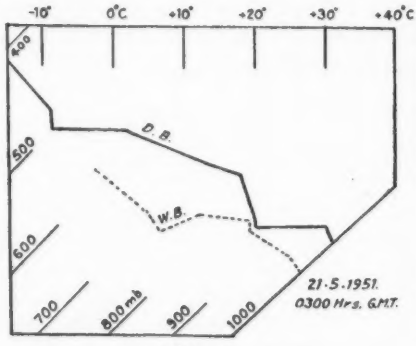

Fig. 8.

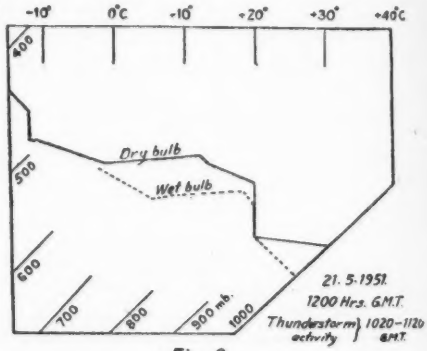

Fig. 9.

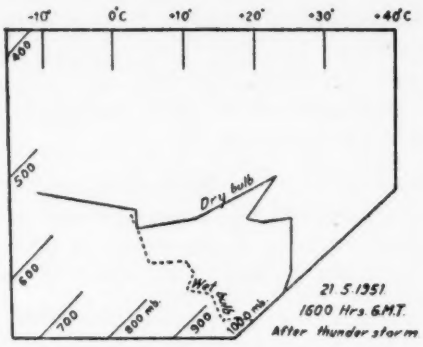

Fig. 10.

thunderstorm activity was over, the drop in temperature at 700 mb. was 7° C., and the cold pool on the ground was noticeable.‡

(*d*) *Waves in the convergence front*[8].—At the discontinuity between the dry and moist air masses, unstable waves develop and are followed by a miniature cyclone which manifests itself in the form of a thunderstorm.

Movement of Nor'westers

The Nor'westers seemingly develop in a haphazard fashion, but there are some which apparently follow some kind of order inasmuch as the activity progresses in particular directions giving the impression of movement with a time-sequence. Such progressive movement can be traced over a distance of 100 miles or more within several hours. As the activity of a single cumulonimbus cell rarely lasts more than an hour, obviously it is not the same cell taking part in a distant Nor'wester a few hours later. Actually, it is a case of successive thunderstorm formation,[11] each thunderstorm inducing the next one in a particular direction, until stable regions are reached. One of the movements from west to east, was found to be correlated with the upper winds at 3–4 Kms. in Bengal.[15] In America similar features were noticed also.[2] The different movements with probable causes are discussed as follows:

(i) Thunderstorms forming in successive positions of a moving cold front. Associated with a western disturbance, the progress is from west to east. The katabatic flow[10, 11] from the base of the hills and through the Surma valley is responsible for movement from the north to south and from northeast to southwest.

‡ In January 1952 issue of the Indian Journal of Meteorology and Geophysics, a case has been reported in which the radio-sonde balloon apparently entered a thunderstorm.[16] The existence of a downdraft at 671 mb. level is noticeable with a marked fall in temperature.

(ii) Cold outflow on the ground,[2, 3, 11] from a parent thunderstorm progressing in a particular direction and inducing more thunderstorms. Usually this movement follows the direction which the main squall takes, but the activity dies out within a few miles in the face of opposing southerly current in Bengal (Fig. 6).

(iii) Cold and moist air at the upper levels left by a parent thunderstorm in the dissipating stage and transported forward under the influence of the prevailing wind inducing more thunderstorms of the high altitude variety in the direction of the upper air stream, *viz.*, W.N.W./E.S.E.[12] (Fig. 7).

(iv) The top portion of a cumulonimbus advances ahead of the base under the influence of stronger upper winds at higher levels, and, as revealed by the formation of Altocumulus *Mammatus* underneath, contains downdrafts and pools of raincooled air (Fig. 11). These overhanging dark tops

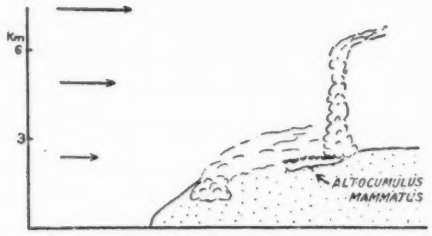

Fig. 11.

are noticeable in the Nor'wester season miles away from the main trunk of the cumulonimbus just before the squall starts. The arrival of the squall soon after the developments apparently indicates that these advancing tops behave like an upper cold front in inducing more thunderstorms along the line of flow of upper winds at those levels. The new thunder clouds so generated have generally a high base to start with, and the tops are hidden from view by the dark layer underneath.

It will be seen from the above, that the action of process (ii) will give rise to a cluster of thunderstorms near each other, while that of (iii) or (iv) will form other groups some distance ahead, leaving inactive regions in between.

ACKNOWLEDGMENT

My thanks are due to the Director-General of Observatories, India, for permission to publish this report. I am also grateful to Mr. J. M. Sil, Deputy Director-General of Observatories (Instruments), for making some radio-sonde instruments available to me for special ascents during 1951

and to the members of Radio-sonde Section, Alipore, Calcutta, for their co-operation in letting off special ascents.

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STUDIES ON TUBER HEMICELLULOSES

Part I. Hemicelluloses from the Tubers of *Asparagus adscendens*

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Hemicelluloses, as has already been reported,[1] form 13·1 per cent. of the carbohydrate portion of the tubers of *Asparagus adscendens* Roxb. Their isolation and examination are reported in this paper.

After the removal of saponins, free sugars, mucilages and pectins by successive treatments with ethyl acetate, 70 per cent. alcohol, hot water and ammonium oxalate solution, the root powder has been extracted for the isolation of the hemicelluloses with 4 per cent. sodium hydroxide according to the method of Norman.[2] Following the procedure of Norris and Precce,[3] the hemicelluloses have been fractionated, and they have yielded only two fractions, namely A_2 and B_2.

Fraction A_2 is an amorphous greyish-white powder. It is soluble in hot water. Its solutions, though viscous, are not mucilaginous, and undergo easy hydrolysis with dilute mineral acids, indicating its hemicellulosic nature.[4] It is composed of xylose, glucose and glucuronic acid in the molecular ratio of 2:1:1.

Fraction B_2 is also amorphous but white in colour. It is also composed of the same sugars and uronic acid as A_2 but in the proportion of 1:1:2.

Experimental

Isolation and fractionation of the hemicelluloses.—From the debarked root powder of *Asparagus adscendens*, saponins, free sugars, mucilages and pectins were removed by extraction respectively with ethyl acetate, 70 per cent. alcohol, warm water and 0·5 per cent. ammonium oxalate solution, and the residual powder was taken for the extraction of the hemicelluloses.

The powder (100 g.) was heated with 4 per cent. sodium hydroxide (500 c.c.) at 45°–50° C. for 2 hours with frequent stirring. After filtering the mixture through a fine muslin, the residue was twice again extracted with the alkali, taking the same volume each time. The total alkaline extract was repeatedly filtered through glass wool, till a clear solution was

obtained. The filtrate was brownish-red in colour. In order to destroy the lignins, if any, the filtrate was treated with 10 g. of sodium hypochlorite and later just acidified with hydrochloric acid to liberate chlorine (method of Norman[2]). After 10 minutes, when no more chlorine was evolved, the hemicelluloses were precipitated by the addition of more acid and excess of alcohol (3 litres). The contents were allowed to stand for 3 hours, and when the hemicelluloses settled down, the supernatant liquid was decanted off and the rest centrifuged. The separated solid was washed first with small quantities of water, then with 60 per cent. alcohol and finally with hot absolute alcohol. The product was dried first in air and then in a desiccator. The yield was 6·1 per cent. on the weight of the debarked root powder taken.

The product was fractionated, following the method of Norris and Preece.[3] It was dissolved in 4 per cent. sodium hydroxide (500 c.c.) and treated with excess of glacial acetic acid, when the solution became turbid. When the solid settled down (6 hours), it was isolated in a centrifuge and washed successively with water and hot alcohol. It (Fraction A) was obtained in a yield of 2·5 per cent. on the weight of the debarked root powder. To the mother liquor (about 600 c.c. in volume), ethyl alcohol (300 c.c.) was added, when Fraction B separated out as a white substance. This fraction too was isolated, washed and dried as Fraction A, and was obtained in 3·6 per cent. yield. The mother liquor, left after the separation of B, did not give any hemicellulose (Fraction C) on treatment with excess of alcohol.

The above fractions were subjected to further fractionation. They were separately dissolved in hot 4 per cent. sodium hydroxide so as to form roughly 1 per cent. solution and filtered through glass wool to get a clear solution. The filtrate was then treated with Fehling's solution at the rate of 30 c.c. per every 100 c.c. However, no precipitate separated out in either case, indicating the absence of Fractions A_1 and B_1. Hence the two hemicelluloses corresponded to Fractions A_2 and B_2 of Norris and Preece. From the alkaline solutions they were recovered by acidification followed by the addition of excess of alcohol, and were purified by repeated dissolution in dilute alkali and reprecipitation by means of acid and alcohol. Ashless products were obtained after three such treatments. Fraction A_2 was obtained in a yield of 2·1 per cent. and B_2 in 3·2 per cent. on the weight of the original debarked root powder.

Hemicellulose A_2.—After purification A_2 was obtained as a greyish-white, amorphous powder, containing 5·2 per cent. of moisture. It was insoluble in alcohol, acetone, ether, etc., but was soluble in hot water, and the solution obtained was somewhat viscous but not mucilaginous. In

aqueous solution (C = 0·4 per cent.) it exhibited a specific rotation of + 15·7° at 18° C.

The hemicellulose responded to naphtho-resorcin test indicating the presence of uronic acid,[5] which when estimated according to the method of Dickson, Otterson and Link,[6] was found to be 24·5 per cent. on the basis of dry material. It did not contain any methoxyl group. Its pentosan content was estimated according to the method of Norris and Resch[7] (applying correction for the furfural which would be liberated from the uronic acid present), and was found to be 49·8 per cent. (zero-moisture basis).

For the identification of the constituent sugars and uronic acids, the purified material (2 g.) was boiled under reflux with 2 per cent. sulphuric acid (150 c.c.) for 2 hours, and the hydrolyzate examined. The latter was neutralized with barium carbonate, filtered and the filtrate analysed, adopting filter-paper chromatography (horizontal migration method of Rao and Beri[8]). Only glucose, xylose and glucuronic acid were detected. The identity of the sugars was confirmed by the preparation of cadmium bromide-cadmium xylonate (characteristic boat-shaped crystals) for xylose and glucosazone for glucose (m.p. 204°–06°). The identity of the uronic acid was also confirmed by the determination of the specific rotation of its barium salt,[9] $[\alpha]_D^{25°} = + 15·64°$, and by the preparation of saccharic acid (isolated as potassium hydrogen saccharate) by oxidation with nitric acid ($d = 1·15$).

Composition of Hemicellulose A_2.—Since the hemicellulose was constituted from only xylose, glucose and glucuronic acid, and since the uronic acid and xylose were found to be nearly 25 and 50 per cent. respectively, the composition of the hemicellulose might be taken to be xylose, glucose and glucuronic acid present in the ratio of 2 : 1 : 1.

Hemicellulose B_2 and Its Composition.—This hemicellulose (Fraction B_2) was white on purification, but was amorphous under the microscope. In aqueous solution (C = 0·67 per cent.), it had a specific rotation of + 21·02° at 18°. It also underwent easy hydrolysis when boiled with dilute sulphuric acid, indicating its hemicellulosic nature. It was examined just as in the case of hemicellulose A_2. The products of hydrolysis were just the same as those obtained from A_2, but the relative proportion was different. In this case xylose, glucose and glucuronic acid were present in the ratio of 1 : 1 : 2.

SUMMARY

The hemicelluloses of the tubers of *Asparagus adscendens* Roxb. have been isolated and chemically examined. They are composed of two fractions, A_2 and B_2 of Norris and Preece designation.

Both the fractions are constituted from the same sugars and uronic acid, *viz.*, xylose, glucose and glucuronic acid but in different proportions. In hemicellulose A_2 the ratio of these components is 2:1:1, while in B_2 it is 1:1:2.

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ROLE OF IONIC DIFFUSION IN THE EXTRACTION OF SOIL SOLUTIONS

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1. Introduction

It has often been suggested that ionic diffusion plays an important role in the extraction of the soil solutions by the displacement method but no satisfactory evidence has ever been established. The water channels in the soil, though quite irregular, may to a first approximation be treated as irregular capillaries. A uniform packing of the soil makes these channels narrow and brings the conditions much nearer to those in a capillary tube. In the present investigation the influence of diffusion on the flow of electrolytes through narrow tubes has been studied and the results obtained are discussed in relation to the extraction of the soil solution.

2. Geometrical Considerations of Stream-Line Flow

Poiseuille's law, discovered in 1840, opened a field for extensive work on the flow of liquids in capillary tubes. It holds good only for streamline flow of liquids the conditions for which were deduced by Reynolds.[1] Under these conditions the liquid contained in any one plane perpendicular to the direction of flow appears after a time on the surface of a paraboloid. The growth of this paraboloid with time is shown in Fig. 1. ABCD is a capillary tube of length, L and radius, R, filled with a liquid L_b. Liquid L_a forms the pressure head at AB and pierces into the tube in the form of a paraboloid displacing the liquid L_b. The volume of liquid that flows out will be equal to the volume of the paraboloid AMB, Fig. 1 *a*. With time, the paraboloid expands and goes on displacing the liquid L_b alone until the tip M touches the open end CD, Fig. 1 *b*. In this position the paraboloid AMB fills the cylindrical tube completely and therefore has a volume half that of the cylinder. Hence 50% of the liquid originally present in the tube should be first displaced before the liquid L_a flows out of the tube. At the open end the streamlines of flow collapse. The disturbance and its range of influence, however, is negligible if the radius of the tube is small in comparison with its length. Further flow of the liquid corresponds to

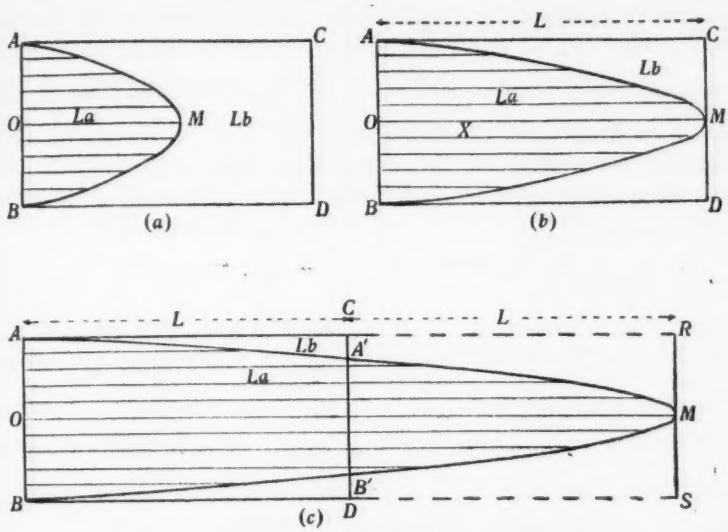

FIG. 1. Stream Line Flow Through a Narrow Tube.

filling of the tube with a part of the paraboloid containing liquid L_a, its size, to a first approximation, increasing as if the flow was continuous, Fig. 1 *c*. It is possible to calculate the volume of the liquid L_b that would be contained in any measured volume of the liquid that is collected at the open end.

The equation for the streamline flow of liquids in narrow cylindrical tubes of length, L, and radius, R, may be written as

$$r^2 = R^2 - v\frac{4\eta L}{P} . \qquad (1)$$

where, v is the velocity of flow of layers at a distance, r, from the centre of the tube, at a given pressure head, P, and η is the coefficient of viscosity of the liquid. This represents the equation of a parabola as shown in Fig. 1. Along the axis of the tube, $r = 0$, and v has maximum value, say, $v.\max.$ If for convenience we choose $v.\max. = L$, *i.e.*, the paraboloid just filling the full length of the tube (Fig. 1 *b*), then

$$R^2 = \frac{4\eta L^2}{P} . \qquad (2)$$

At any intermediate position X, marked between O and M if $OX = \frac{L}{n}$ where n is an integer, r_x the radius of the parabola at X is given by

$$r_x^2 = R^2\left(1 - \frac{1}{n}\right) . \qquad (3)$$

Imagine an extension in the length of the tube as shown in Fig. 1 *c*. Here AR = 2L, twice the length of the tube. The radius of the section of the paraboloid at A′B′, the open end works out from equation 3, as $\frac{R}{\sqrt{2}}$ and the volume of the paraboloid A′MB′$=\frac{1}{4}\pi R^2 L$. If V is the volume of the tube of length, L, the volume of the paraboloid AMB (Fig. 1 *c*) will also be equal to V, and the volume of AA′B′B, a part of the paraboloid is then given by

$$\text{Vol. AA'B'B} = V - \frac{V}{4} = \frac{3V}{4} .$$

Thus when the paraboloid has been assumed to have been extended up to a length 2 L, the liquid that would be collected at the open end AB would be V c.c. and would contain $\frac{3V}{4}$ c.c. of liquid L_b. Similarly, if the paraboloid is to have been extended up to a length 3 L, along the axis of flow, the total volume of the liquid $\frac{3V}{2}$ c.c. collected at the open end would contain $\frac{5V}{6}$ c.c. of the liquid L_b. In general, the volume of the liquid L_b that gets displaced may be given by the equation

$$V_{L_b} = \frac{\pi}{2} R^2 \left(2L - \frac{L}{n}\right) , \qquad (4)$$

where, $n \geqq 1$ and represents the number of lengths of the tube over which the paraboloid is supposed to have been extended. Table I gives the calculated volumes of the liquid that flow out and the corresponding volumes of liquid L_b that it would contain.

TABLE I

Volume of the Liquid Collected at the Open End and the Volume of the Liquid L_b Present in it, Calculated from the Geometry of the Tube

Total Volume of the Liquid Collected	Volume of the Liquid L_b displaced
V/2	V/2
V	3V/4
3V/2	5V/6
2V	7V/8
5V/2	8V/9
3V	9V/10

If there is no diffusion taking place between the liquids L_a and L_b, the results in Table I should hold good irrespective of (*a*) the velocity of flow within the streamline limits and (*b*) the dimensions of the tube.

3. Experimental Arrangements

Two narrow glass tubes of about a metre in length and about three and two millimetres diameter respectively were used in the present investigation. Each tube was slightly bent at either end as shown in Fig. 2, to facilitate

Fig. 2. Apparatus for the Study of Diffusion in the Stream Line Flow of Liquids.

easy filling of the liquid before starting the experiment and collection of the liquid during the course of the flow. The end A of the tube projects into a wider tube and can be sealed at any desired height. T is a side tube to regulate the level of the liquid that flows in continuously from a burette. The experimental tube was filled with liquid L_b between the marks O and B. Sodium nitrate and sodium bicarbonate solutions of the same concentrations were taken as liquids L_a and L_b respectively. The choice of these two electrolytes was based on two considerations:—

(*a*) The densities of the sodium nitrate and sodium bicarbonate solutions of the same concentration are nearly the same so that they do not mix due to density differences.

(*b*) One of these electrolytes, sodium bicarbonate solution can be easily estimated in the presence of the other, *viz.*, sodium nitrate solution.

N/5 concentrations were found sufficient with tube No. 1 of 3·04 mm., diameter, while N/2 concentrations were found necessary with tube No. 2 of 1·98 mm. diameter. In the beginning the amount of sodium bicarbonate solution filling the tube between O and B was estimated against N/20 hydrochloric acid. In tube No. 1, 29·90 c.c. of acid was required while in tube No. 2, 31·10 c.c. had to be used.

The capillary tube filled with the sodium bicarbonate solution between the marks O and B was kept horizontally. The end B was temporarily

closed as to hold the liquid and sodium nitrate solution of the same concentration was then made to run gently into the wider tube, so that it would fill the space between O and A and gradually rise in level up to the tap, T, where a constant pressure head could be maintained. The end B was then opened and the liquid flowing out of the horizontal tube OB, was collected in fractions into beakers of known weight. The velocity of flow was regulated by suitably altering the pressure head on the side A, of the tube. At each regulated velocity of flow, the liquid that would flow at the open end, B, was collected in fractions of approximately known weight into twelve beakers. The weight of the liquid collected in each beaker is proportional to the volume of the liquid displaced. Sodium bicarbonate solution present in each fraction of the liquid collected was estimated against N/20 hydrochloric acid. The amount of bicarbonate solution present in any given beaker is proportional to the hydrochloric acid required to neutralise it.

4. RESULTS

The total weights of the liquid collected at different stages of the flow are plotted against the total volumes of N/20 hydrochloric acid required to neutralise the respective weights of the liquid collected. The results obtained with tubes 1 and 2 are recorded in Figs. 3 and 4 respectively.

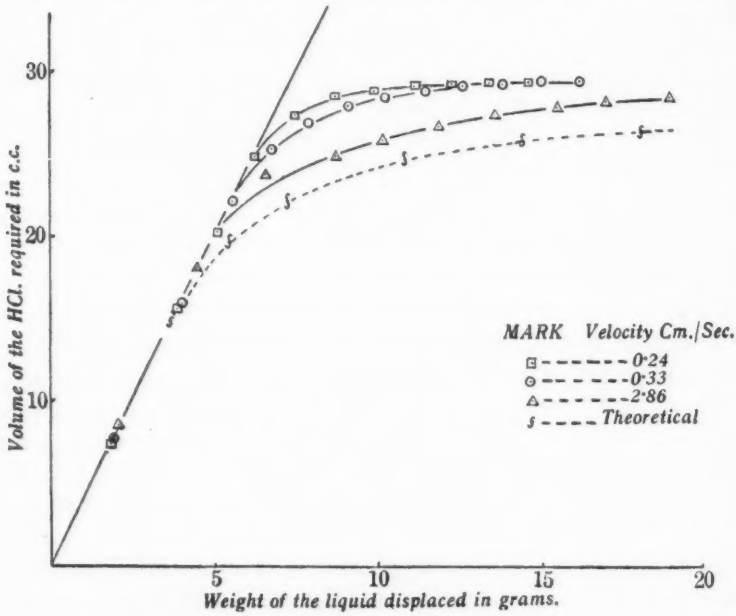

FIG. 3. Length of the tube = 98·0 cm. Diameter of the tube = 3·04 m.m. Volume of HCl required to neutralise the $NaHCO_3$ Solution Completely filling the tube = 29·90 c.c.

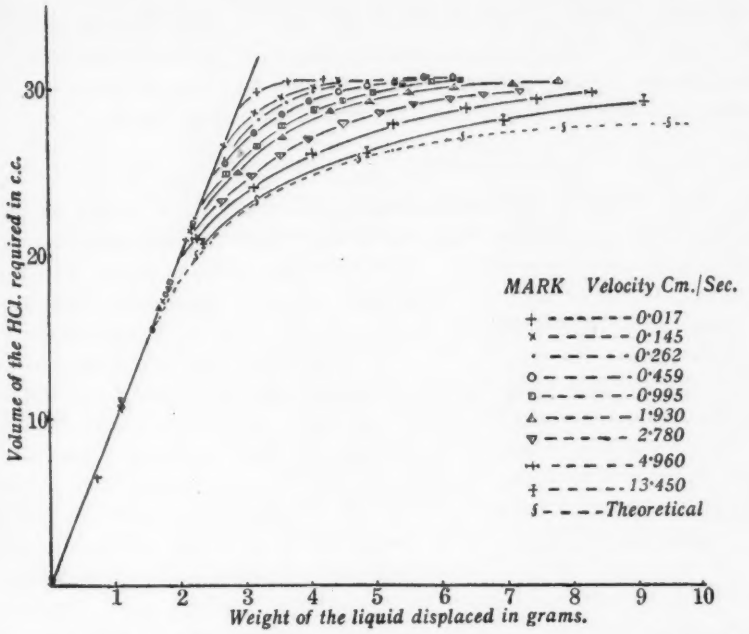

FIG. 4. Lengh of the tube = 100·0 cm. Diameter of the tube = 1·98 m.m. Volume of HCl required to neutraise the $NaHCO_3$ Solution Completely filling the tube = 31·10 c.c.

Using tube No. 1, only three different velocities of flow were tried while with tube No. 2 observations at nine different velocities of flow were recorded. The results expected from streamline flow considerations, as calculated from Table I, are plotted as broken curves while the experimental points are marked continuous. All the velocities recorded were kept within the limits of streamline flow.

It may be seen in Figs. 3 and 4 that up to a volume of liquid displaced equal to half the volume of the capillary tube between O and B, there is a linear relation, as expected, between the total volume of the liquid collected and the volume of the sodium bicarbonate solution displaced, irrespective of the velocity of flow. For greater volumes of the liquid collected, however, the curves for different velocities of flow spread out and the lower the velocity of flow, the greater is the sodium bicarbonate solution displaced. For the same weight of the liquid collected, the curve corresponding to a higher velocity of flow is closer to that drawn from geometrical considerations than the one corresponding to a lower value. With decreasing values of the velocity of flow, however, the linear part of the curve increased and

at an average velocity of 0·017 cm. per sec., studied (Fig. 4) as high as 95% of the sodium bicarbonate solution originally present in the tube is displaced before sodium nitrate solution would flow out of the tube. This observation cannot be explained by Poiseuille's flow alone.

5. DISCUSSION OF THE RESULTS

All the velocities of flow maintained in the tubes are well within the streamline flow; even the highest velocity studied with tube No. 2, *i.e.*, 13·45 cm., per sec., is a fraction of the limiting velocity for a change from the stream-line flow into turbulent flow. If the liquids flow according to the geometrical considerations discussed, the results irrespective of the velocities studied should fall in a line with the theoretical values drawn in Figs. 3 and 4. The spread of the experimental curves and their increasing deviation from the theoretical curve with decreasing velocities of flow can be explained as due to ionic diffusion between the two liquids inside the tube during the course of flow. As the sodium nitrate solution which forms the pressure head pierces through the sodium bicarbonate solution, in the form of a paraboloid, diffusion takes place on the common surface of contact between the two liquids. During this process bicarbonate ions diffuse towards the centre of the tube and thus pick up higher and higher speeds while nitrate ions diffuse away from the centre loosing their speed. The total amount of the ion diffused increases with increasing time of contact between the two liquids. Hence the smaller the velocity of flow the greater would be the quantity of the bicarbonate ion diffused towards the centre of the tube and would be delivered at the open end. For the smallest velocity of flow studied, this diffusion is so great that the bicarbonate ion appears as if it is bodily pushed out before the nitrate ion comes out of the tube.

The curves obtained for different velocities of flow in a given tube depend on the parameters given below:—

(*a*) The coefficient of diffusion D;

(*b*) The radius of the tube, r and

(*c*) The time, t, where $t = \frac{L}{v}$, L being the length of the tube and v, the mean velocity of flow.

A rigorous mathematical treatment of the problem seems to be complicated. The curves drawn in Figs. 3 and 4 however, depend upon a non-dimensional constant, one for each curve, containing the parameters involved

in their measurements. From a consideration of the dimensions the constant, K may be written as

$$K = \frac{D}{r^2} \cdot \frac{L}{v} .$$

The importance of this non-dimensional constant is that the nature of the curve remains the same with different sets of parameters which give the same value of the constant. Thus keeping the values of D and L constant, a change in the value of r, should have a corresponding change in v, such that

$$\frac{r_1^2}{r_2^2} = \frac{v_2}{v_1} .$$

In the experimental curves drawn in Figs. 3 and 4, the lenghts of the tubes are nearly the same; the value of D, however, differs slightly from one set to the other as two different concentrations had to be used. The temperature of the experiments also was slightly varying. Accounting for these changes, the curves in Figs. 3 and 4 seem to fairly satisfy the non-dimensional constant. It is possible to use this constant to determine the value of the order of the diffusion coefficient if the other parameters are measured.

It follows from the above considerations that in soils where the water channels are fairly uniform and narrow it is possible to have velocities much higher than in the narrow tubes and yet to get the soil solution displaced by the displacing liquid. The uniformity of the water channels depends on the homogeneous packing of the soil; any big channels left in it will allow the water to flow through, thus diluting the soil solution extracted. In this connection the experiments of the earlier investigators on the extraction of the soil solution are interesting.

The results obtained by Lawes, Gilbert and Warington[2] with drainage solutions can be explained as due to ionic diffusion. In one of the experiments where air-dried arable soil was wetted from the top, they observed that 75% of the diffusable salts were removed in about 50 c.c. of the drainage water. This may be explained as follows: The soil originally contains some moisture and the more easily soluble and diffusable salts are in the ionic form. As the water slowly percolated from the top, these ions diffuse into the porespace acquire greater speed and appear as if they were being pushed down by the percolating solution. Subsequent work of Burd and Martin[3] shows that water could be used to displace the soil solution by the process of percolation and successive displaced solutions in the first few fractions collected had equal concentrations. The concentration thus measured in each case was the same as that of the liquid obtained without the use of

displacing water. In all these cases the ionic diffusion is responsible for the soil solutions to be displaced before the displacing liquid would appear.

6. SUMMARY

Flow of electrolytes, one displacing the other in capillary tubes, has been studied under different velocities within the limits of streamline flow. The amounts of the displaced and displacing electrolytes present in a known volume of the solution, collected at the open end, were evaluated from an equation deduced from the geometrical considerations of the tube. Sodium nitrate solution was used as pressure head to displace sodium bicarbonate solution of the same concentration initially filling the whole tube. The amount of the displaced sodium bicarbonate solution present in any given volume of the liquid collected, was found to be closer to the theoretical value, only at higher velocities of flow; with decreasing velocities of flow, however, its value increased and deviated more and more from the expected theoretical value. This deviation is explained as due to the influence of ionic diffusion taking place between the bicarbonate and nitrate ions of the displaced and displacing liquids. At the lowest velocity of the flow studied, as high as 95% of the bicarbonate solution was displaced, before the nitrate solution could come out of the tube, as if it was bodily pushed out by the displacing liquid.

From the results obtained it could be deduced that in soils of uniform packing with fine capillary pores, it is possible to have velocities of flow much higher than those used in the capillaries studied, and yet get the soil solution displaced. This concept of ionic diffusion thus explains the principle underlying the experiments of Burd and Martin, for the extraction of soil solutions, using water as the displacing liquid.

The above work was carried out at the Rothamsted Experimental Station and the authour desires to record his grateful thanks to Dr. R. K. Schofield, Head of the Soil Physics Department, for his helpful suggestions and discussions during the course of this investigation.

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NUCLEAR OXIDATION IN FLAVONES AND RELATED COMPOUNDS

Part XXXVIII. A Transformation of Visnagin to Kellin

By S. K. Mukerjee and T. R. Seshadri, F.A.Sc.
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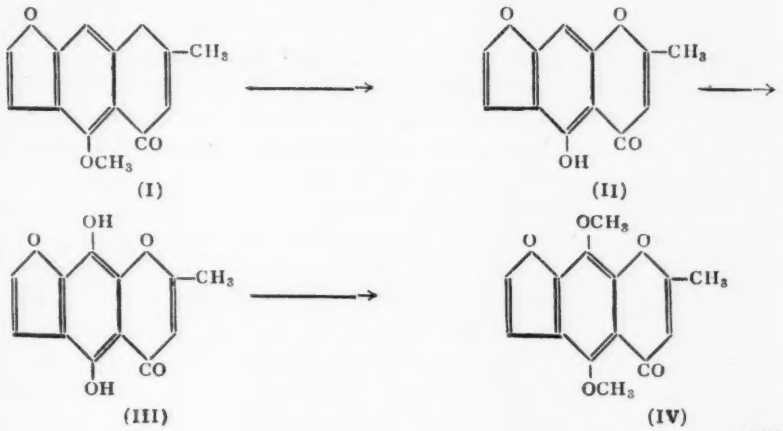
Received March 31, 1952

The main crystalline components of the seeds of *Ammi visnaga* are (*a*) kellin, (*b*) visnagin and (*c*) chellol glucoside; of these, the first is highly valuable therapeutically, the second has much less activity and the third none. But they are related in their chemical structure; consequently methods of conversion of (*b*) and (*c*) into (*a*) will be useful. Already a successful method of conversion of chellol into visnagin has been described by Geissman[1]; a yield of 25% is claimed. Although the next stage (*b* to *a*) has been worked out by Schönberg and Badran,[2] the reported yield of the final product is very poor, being only 3%; further it involves six steps.

It was therefore felt desirable to work out a better method for the conversion of visnagin to kellin. One such is described in this paper. It utilises the nuclear oxidation of nor-visnagin with alkaline persulphate to nor-kellin and subsequent methylation of it. Not only does this reduce the number of the stages to four but it increases the yield of the final product appreciably.



Preparation of nor-visnagin proceeds very satisfactorily by means of hydrochloric acid giving about 80% yield.[2] In the next stage, persulphate oxidation gives somewhat low yields (12%). Methylation of nor-kellin to kellin was originally carried out by Schönberg and Badran,[2] using methyl iodide giving an yield of 50%. When it is done using methyl sulphate the yields are much better (91%). Thus the minimum yield of kellin from visnagin has been raised from about 3% to about 9%.

In the course of experiments described above, it has been possible to effect partial methylation of nor-kellin in the eight position. This substance is identical with the product obtained by partial demethylation of kellin with 50% hydrochloric acid. It is therefore formulated as an 8-methoxy compound and its properties are in accordance with this.

The term nor-kellin was originally used by Murti and Seshadri[3] for the parent dihydroxy compound obtained by the demethylation of kellin without involving isomeric change. Later the term has been used by Schönberg and Sina[4] to designate also the lower homologue of kellin which does not have a methyl group in 2-position. It seems to be desirable to restrict its use to only one compound, that is the parent dihydroxy furano chromone related to kellin. We suggest that the derivatives lacking the 2-methyl group may be called homo-kellin.

EXPERIMENTAL

Oxidation of nor-visnagin to nor-kellin (II→III)

Nor-visnagin[2] (1 g.) was dissolved in pure pyridine (15 c.c.) and to the brown solution was added aqueous sodium hydroxide (0·85 g. in 15 c.c. of water), when the deep yellow sodium salt separated out; some of it dissolved on the addition of more pyridine (10 c.c.). To this suspension which was mechanically stirred and maintained at 15–20°, was added dropwise a saturated aqueous solution of potassium persulphate (2 g. in 35 c.c.) during the course of six hours. The solid gradually went into solution and the colour of the solution which was deep yellow at first changed to deep red in about 3 hours. The stirring was continued for two hours more by which time the whole of the sodium salt dissolved and the solution was left overnight at room temperature. Next day it was made just acidic to congo red when a buff coloured precipitate separated out. This was filtered (it was not unchanged nor-visnagin) and the filtrate was extracted with ether twice to remove impurities. The aqueous solution was then made strongly acidic with concentrated hydrochloric acid (35 c.c.), sodium sulphite (4 g.) was added and the mixture heated in a boiling water-bath for 30 minutes. It was then cooled and thoroughly extracted with ether. On evaporating the ether extract a yellow

product (0·12 g.) was left behind which crystallised from alcohol as yellow rectangular prisms melting at 281–83°. A mixed melting point with an authentic sample of nor-kellin[3] prepared from kellin was undepressed. An alcoholic solution of it gave with ferric chloride a deep green colour which changed to reddish brown with excess. The oxidation was repeated using more pyridine in order to avoid precipitation of solid at any stage and the alkali was added slowly along with the persulphate. But there was no significant increase in yield.

The acetate of nor-kellin was prepared by heating a mixture of nor-kellin (50 mg.), acetic anhydride (2 c.c.) and pyridine (1 drop) at 140–45° for 2 hours. It was then poured into ice-water and the white solid that separated after some time was collected and crystallised from a mixture of ethyl acetate and petrol when it was obtained as colourless rectangular prisms melting at 174–75°. A sample of acetate prepared from an authentic sample of kellin had the same melting point and the mixed melting point of the two samples was undepressed (Found: C, 61·2; H, 3·9; $C_{16}H_{12}O_7$ requires C, 60·8; H, 3·8%).

Methylation of nor-kellin to kellin (III—IV)

Nor-kellin (1 g.) was suspended in dry acetone (100 c.c.) and treated with dimethyl sulphate (1·5 c.c.) and ignited potassium carbonate (6 g.) and the mixture was heated under reflux for 15 hours. The acetone solution was filtered and the potassium salts were washed twice with hot acetone. Acetone was removed from the filtrate and washings and to the residual brownish oily substance, water (100 c.c.) was added to decompose excess of dimethyl sulphate. The crystalline mass which separated on keeping overnight was collected and crystallised twice from dilute alcohol when it separated as colourless rectangular prisms melting at 152–53° alone or when mixed with an authentic sample of kellin. Yield, 0·91 g.

2-*Methyl*-5-*hydroxy*-8-*methoxy-furano*-(3′ : 2′ : 6 : 7) *chromone*

(i) *Partial methylation of nor-kellin.*—Nor-kellin (0·3 g.) was dissolved in dry acetone (50 c.c.), methyl iodide (0·5 c.c.) and ignited potassium carbonate (4 g.) were added and the mixture refluxed in a water-bath for one and a half hours. The acetone solution was then filtered and the potassium salts were washed several times with hot acetone. The inorganic salts did not retain any of the product. The combined filtrate and washings were concentrated when a pale yellow product crystallised out. This was filtered and recrystallised from ethyl acetate when it separated as golden yellow long thick rectangular prisms melting at 200–02°. Yield, 0·21 g. It gave a permanent

deep green colour with ferric chloride and a golden yellow solution in concentrated sulphuric acid (Found: C, 63·8; H, 4·2; $C_{13}H_{10}O_5$ requires C, 63·4; H, 4·1%).

(ii) *Partial demethylation of kellin.*—Kellin (0·5 g.) was dissolved in a hot mixture of concentrated hydrochloric acid (8 c.c.) and water (8 c.c.) and the solution refluxed on a wire-gauze for one and a half hours. A deep red solution was obtained at first and after 15 minutes a yellow precipitate began to form. The mixture was then diluted with water (20 c.c.), cooled and the solid product filtered and washed free from acid. It crystallised from ethyl acetate as golden yellow rectangular prisms melting at 200–02° alone or when mixed with the sample obtained in (i) above. Yield, 0·35 g.

The acetate was prepared by acetic anhydride pyridine method and crystallised from ethyl acetate when it was obtained as colourless stout rectangular prisms melting at 173–75° (Found: C, 63·1; H, 4·3; $C_{15}H_{12}O_6$ requires C, 62·5; H, 4·2%).

SUMMARY

A new method of conversion of visnagin into kellin is described. It involves only three steps and gives much better yields. Nor-visnagin is subjected to nuclear oxidation with alkaline persulphate to yield nor-kellin which is conveniently methylated to kellin by means of dimethyl sulphate and potassium carbonate in acetone solution.

Our thanks are due to the Council of Scientific and Industrial Research for a grant-in-aid and to Dr. W. G. Bywater of S. B. Pennick & Co., New York (U.S.A.), for a gift of visnagin and kellin used in this investigation.

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2. Schönberg and Badran .. *Ibid.*, 1951, **73**, 2960.
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4. Schönberg and Sina .. *J. A. C. S.*, 1950, **72**, 1611.

NUCLEAR OXIDATION IN FLAVONES AND RELATED COMPOUNDS

Part XXXIX. Occurrence of Nuclear Oxidation in the Biogenesis of Lichen Acids

By K. Aghoramurthy and T. R. Seshadri, F.A.Sc.

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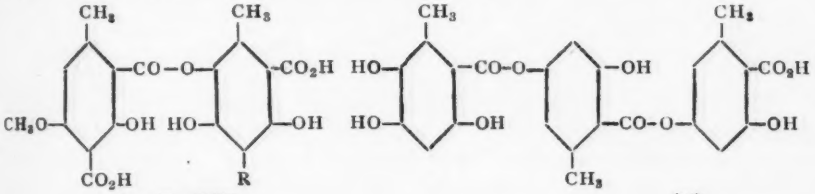
Received April 9, 1952

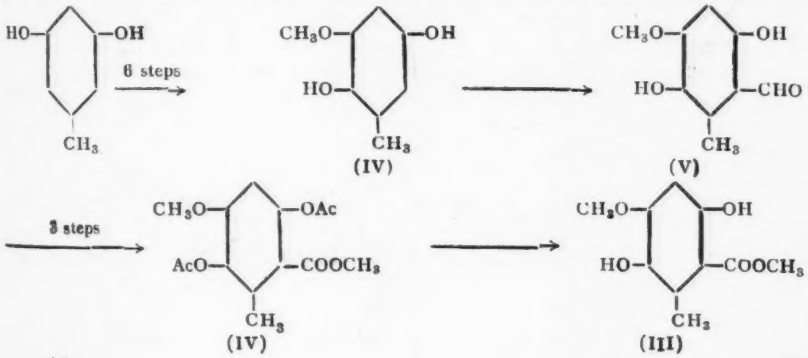
In an earlier paper[1] on the theory of biogenesis of lichen depsides and depsidones, examples of nuclear oxidation were given. There are cases both of para as well as of ortho nuclear oxidation of the orsellinic acid unit. The following represent examples of para oxidation: thamnolic acid (I *a*), hypo-thamnolic acid (I *b*) and hiascinic acid (II).



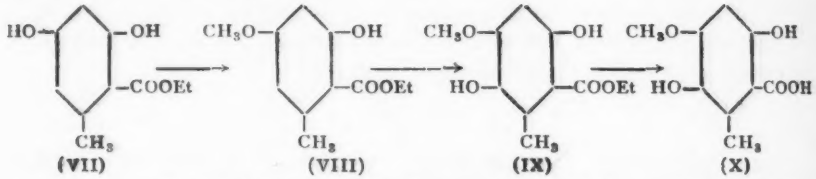
I *a*, R=CHO
b, R=CH_3

(II)

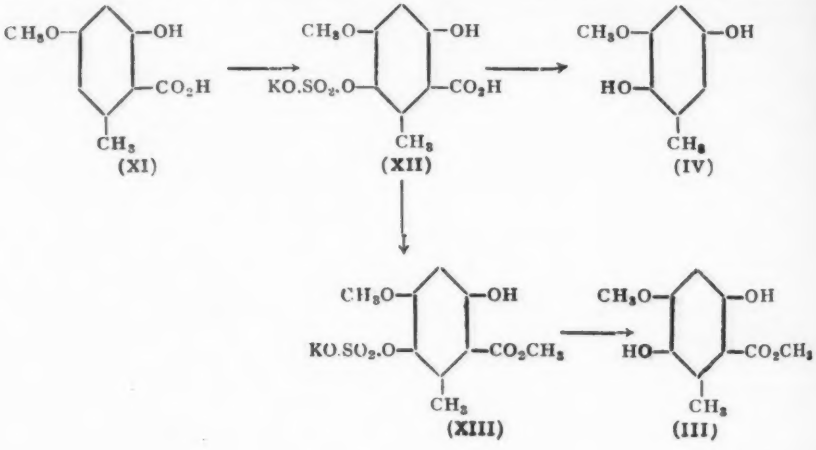
Though some of the units present in them had been synthesised by other methods, application of the methods of nuclear oxidation following the scheme of biogenesis usually offer comparatively easier approach. The syntheses of a few important examples as representatives of the above types are therefore considered here. The first is 5-hydroxy everninic ester (III) synthesised earlier by Asahina and Kusaka[2] employing the following steps:



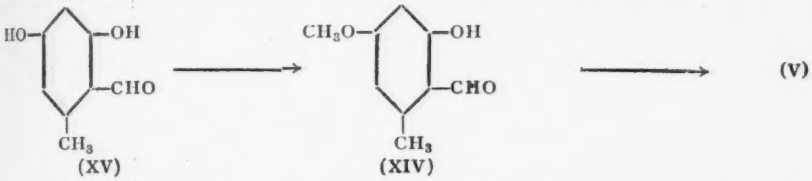
The corresponding ethyl ester (IX) has now been prepared starting from ethyl orsellinate (VII) obtained by the fission of lecanoric acid which was isolated from *Parmelia tinctorum*. It is partially methylated using one mole of methyl sulphate and excess of potassium carbonate in acetone solution to yield ethyl everninate (VIII). Nuclear oxidation with alkaline persulphate yields the quinol ester (IX) which undergoes hydrolysis with 15% sodium hydroxide solution to produce 5-hydroxy everninic acid (X). The yields are satisfactory in the above-mentioned stages of synthesis. It should be stated here that the persulphate oxidation in alkaline medium does not hydrolyse the ester group. This stability has been found to be present in ortho-toluic esters in general.[3]



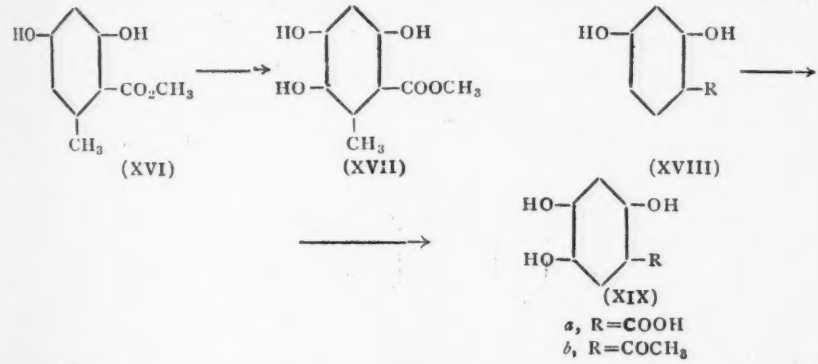
The use of everninic acid (XI) for nuclear oxidation with persulphate yielded interesting new results. A sparingly soluble potassium salt of the para hydroxy phenyl sulphate (XII) could be isolated. Its hydrolysis with hydrochloric acid was accompanied by decarboxylation also producing 2:5-dihydroxy-4-methoxy toluene (IV). The above decarboxylation could be avoided by esterifying the carboxyl group of the potassium salt and then treating the ester (XIII) with hydrochloric acid. By this means the methyl ester of 5-hydroxy everninic acid (III) could be obtained in satisfactory yield.



As a purely synthetic starting point the nuclear oxidation of everninic aldehyde (XIV) is useful. It is well known that carboxylation of orcinol yields only para orsellinic acid and the synthesis of orsellinic acid has to pass through the aldehyde (XV) as intermediate. This aldehyde can be partially methylated to everninaldehyde (XIV) and subsequently subjected to persulphate oxidation to form 5-hydroxy everninaldehyde (V). As mentioned above, this was made originally by Asahina and Kusaka[2] starting from the quinol (IV), and they also oxidised its acetate with potassium permanganate in acetone solution to form the corresponding carboxylic acid.



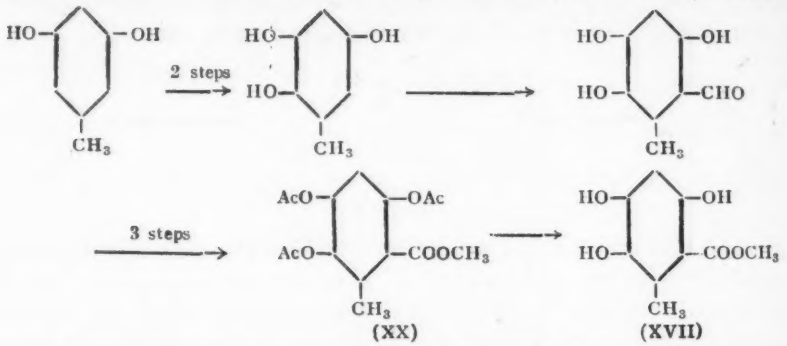
In the earlier stages of the present investigations everninic acid, its ester and aldehyde were employed instead of orsellinic acid and related compounds since it was felt that the protection of one of the hydroxyl groups was essential for the success of the nuclear oxidation or at least for the purpose of obtaining satisfactory yields. At a later stage the oxidation of methyl orsellinate (XVI) itself has been carried out. It is found to proceed fairly satisfactorily and thus the methyl ester of 5-hydroxy orsellinic acid (XVII) could be directly and conveniently obtained. Here again the ester group does not undergo hydrolysis during the oxidation under alkaline conditions. Further this is an example where persulphate oxidation proceeds satisfactorily in spite of the presence of two free hydroxyl groups in the original molecule. Similar examples of nuclear oxidation are the oxidation of β-resorcylic acid (XVIII *a*)[4] and resacetophenone (XVIII *b*)[5] to



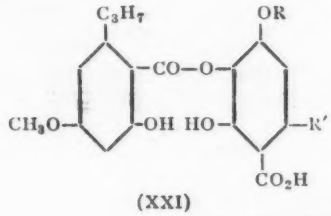
a, R=COOH
b, R=$COCH_3$

5-hydroxy resorcylic acid (XIX *a*) and 5-hydroxy resacetophenone (XIX *b*) respectively. However the yields of the oxidation products in these cases are very low. Obviously the higher yield in the oxidation of orsellinic ester could be traced to the comparatively higher stability of this structure under the conditions of the reaction.

The earlier synthesis of the above-mentioned 5-hydroxy orsellinic ester (XVII) (Asahina and Kusaka[2]) starting from orcinol is indicated below:

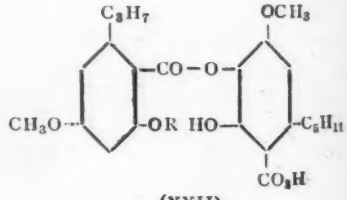


As examples of the occurrence of ortho-oxidation, *i.e.*, introduction of a hydroxyl group in the 3-position of the orsellinic acid unit, could be cited the following: sekikaic acid (XXI *a*), ramalinolic acid (XXI *b*), homosekikaic acid (XXII *a*), boninic acid (XXII *b*) and diploschistessic acid (XXIII).



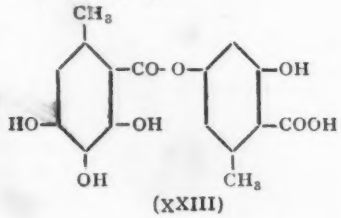
(XXI)

a, R=CH3, R'=C3H7
b, R=H, R'=C5H11



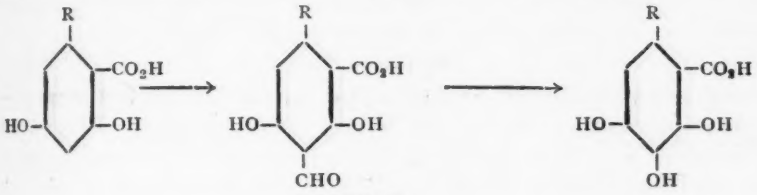
(XXII)

a, R=H
b, R=CH3



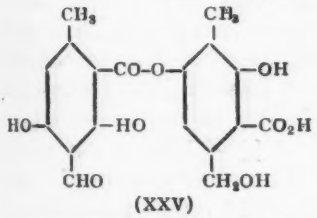
(XXIII)

The first four contain the oxidised unit on the right halves of the depside molecules and the products are meta depsides owing to the greater stability of this type of structure. On the other hand, the last one represents ortho nuclear oxidation in the left half. According to the theory of ortho nuclear oxidation discussed in connection with the anthoxanthins,[6] orsellinic acid derivatives with the aldehyde group in the 3-position (XXIV) would represent intermediate stages. The aldehyde group is found for instance in barbatolic acid (XXV) and atranorin (XXVI) and corresponding hydroxy units are present in sekikaic, homo-sekikaic, ramalinolic and boninic acids. These aldehydes could then be considered to undergo oxidation (similar to Dakin's reaction) to yield 3-hydroxy orsellinic acid derivatives.

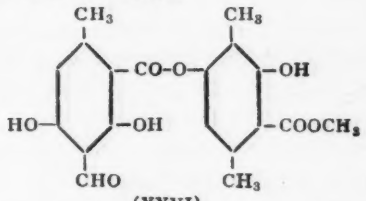


(XXIV)

R=CH_3, C_3H_7, C_5H_{11}, C_7H_{15} or $CH_3-CO-C_5H_{11}$

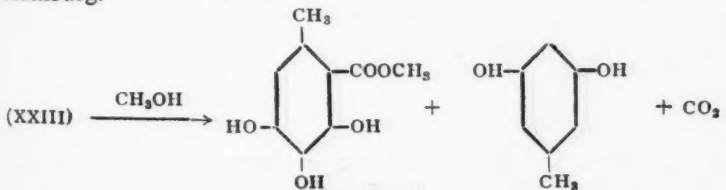


(XXV)



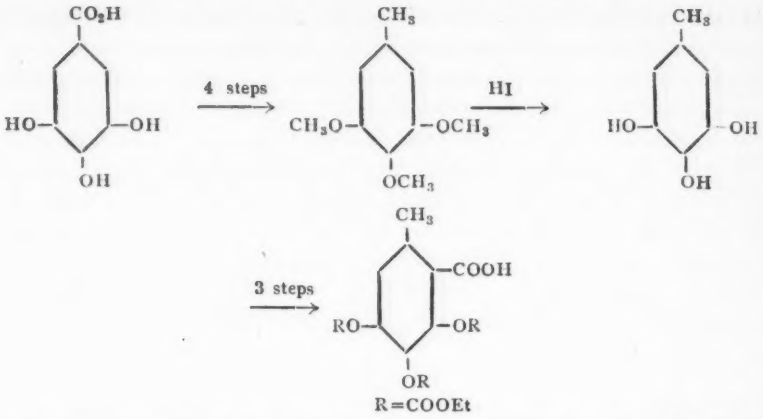
(XXVI)

To illustrate the validity of the above-mentioned scheme, the synthesis of 3-hydroxy orsellinic ester (XXVII) has now been carried out. The ester was first prepared by the methanolysis of diploschistessic acid by Koller and Hamburg.[7]

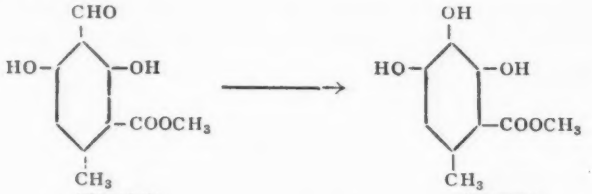


(XXVII)

Later on Asahina and Yasue[8] synthesised the derivatives of the acid starting from gallic acid and following the procedure indicated by the scheme given below;



The ortho oxidation method now employed involves as the first stage the preparation of hæmatommic ester (XXVIII). It is a product of fissicn of atranorin which is widely present in *Parmelia tinctorum*. It can be prepared synthetically from methyl orsellinate. The earlier method of St. Pfau,[9] and Robertson and Stephenson[10] using hydrogen cyanide gave a mixture of methyl hæmatommate and its isomer in poor yield. Much better yields of methyl hæmatommate as the sole product were obtained by Sastri and Seshadri[11] who employed zinc cyanide and anhydrous aluminium chloride according to the general procedure of Shah and Laiwalla,[12] and were later confirmed by the experiments of Whalley.[13] Methyl hæmatommate undergoes Dakin's oxidation smoothly to yield about 40% of 3-hydroxy orsellinic ester which agrees fully with the description of Koller and Hamburg.[7] This nuclear oxidation therefore renders the synthesis of 3-hydroxy orsellinic acid and its ester quite easy.

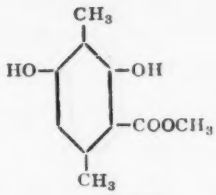


(XXVIII) (XXVII)

At this stage may be recalled the original suggestion[1] regarding the biogenesis of C-methyl groups in the 3-position of orsellinic acid units leading to the formation of β-orcinol derivatives. Carbinol groups were considered to be the precursors and they underwent reduction to methyl groups. A number of examples of this type have already been given. The reduction

of methyl hæmatommate by the Clemmenson method to β-orcinol carboxylic ester (XXIX) was reported by Whalley.[13]

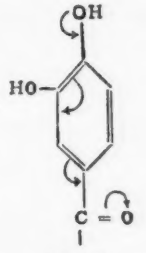
(XXVIII) ⟶



(XXIX)

Taking into consideration all the transformations discussed above it follows conclusively that CH_3, CH_2OH, CHO, COOH and OH groups in the 3-position of an orcinol unit in a lichen depside are clearly interrelated as indicated in Part XXVI[6] of this series.

As mentioned earlier, a meta depside is more stable than a para depside and the former tends to be formed even by the isomerisation of the latter. No definite explanation has so far been offered. This phenomenon can be understood on the following basis. As a result of the electromeric polarisation initiated by the C = O group in (XXX) the hydroxyl in 4-position will become most acidic whereas the one in the meta position will be unaffected. Consequently an ester involving the para hydroxyl will have more of the instability of an anhydride whereas the meta depside will be more akin to an ester, and thus be more stable.



(XXX)

Experimental

Ethyl everninate (VIII)

This is conveniently made by the partial methylation of ethyl orsellinate.

A solution of ethyl orsellinate (6·0 g.) and methyl sulphate (3·2 c.c.) in dry acetone (100 c.c.) was treated with anhydrous potassium carbonate (10·0 g.) and the mixture gently refluxed for 6 hours. The potassium salts

were filtered and washed with warm acetone. Distillation of the acetone filtrate yielded ethyl everninate which crystallised out of alcohol as colourless prisms melting at 73–74°. It gave a blue colour with ferric chloride solution. A bluish green colour was developed in contact with concentrated nitric acid. Robertson and Stephenson[13] recorded a melting point of 72°.

Ethyl 2: 5-*dihydroxy*-4-*methoxy*-6-*methyl benzoate* (*IX*)

To a solution of ethyl everninate (6·3 g.) in aqueous sodium hydroxide (10%, 60 c.c.) cooled to 10° was added dropwise an aqueous solution of potassium persulphate (9·0 g. in 150 c.c.) with stirring in the course of 4 hours. After standing for 24 hours at room temperature, the solution was acidified to Congo-red with hydrochloric acid and extracted with ether twice to remove the unreacted compound. The aqueous solution was treated with concentrated hydrochloric acid (40 c.c.) and sodium sulphite (5·0 g.) and warmed in a water-bath at 80° for 30 minutes. The solution was cooled and extracted with ether. The ether extract was dried and distilled yielding ethyl 2: 5-dihydroxy-4-methoxy-6-methyl benzoate. Yield, 2·5 g. It crystallised from alcohol as colourless flat needles and rectangular prisms melting at 106–07°. With alcoholic ferric chloride it gave a blue colour which quickly changed to green and finally faded. It did not give any blue colour with concentrated nitric acid (Found: C, 58·1; H, 6·2; $C_{11}H_{14}O_5$ requires C, 58·4; H, 6·2%).

The diacetate was prepared by refluxing it with acetic anhydride and pyridine for 1 hour, and it crystallised from alcohol as colourless rectangular plates and needles melting at 134–35° (Found: C, 57·5; H, 5·7; $C_{15}H_{18}O_7$ requires C, 58·1; H, 5·8%).

2: 5-*Dihydroxy*-4-*methoxy*-6-*methyl benzoic acid* (*X*)

The ethyl ester (IX) (0·5 g.) was dissolved in 15% sodium hydroxide solution (5 c.c.) and kept at 80–100° for 30 minutes. The cooled solution was acidified with dilute hydrochloric acid. The precipitate was taken up in saturated sodium bicarbonate solution (10 c.c.), filtered from traces of unchanged ester and finally acidified. On crystallisation from benzene-ligroin mixture, 2: 5-dihydroxy-4-methoxy-6-methyl benzoic acid was obtained as colourless stout rectangular prisms and prismatic needles melting at 172–73° (decomp.) (Found: C, 54·3; H, 5·6; $C_9H_{10}O_5$ requires C, 54·5; H, 5·1%).

Everninaldehyde (*XIV*)

This was made earlier by Robertson and Stephenson[14] by the partial methylation of orsellinic aldehyde using methyl iodide and potassium carbonate in acetone solution. It is now found that the preparation is con-

veniently carried out by using orsellinic aldehyde (1 mole), dimethyl sulphate (1·1 mole) and excess of anhydrous potassium carbonate and refluxing the mixture for 6 hours in acetone solution. Everninaldehyde gave a bluish green colour with concentrated nitric acid.

2:5-Dihydroxy-4-methoxy-6-methyl benzaldehyde (V)

Everninaldehyde (5·7 g.) was dissolved in pyridine (10 c.c.) and aqueous sodium hydroxide (10%, 70 c.c.) and the solution cooled in ice. A solution of potassium persulphate (10 g. in 250 c.c.) was added dropwise to the above solution with stirring in the course of 4 hours. After 24 hours, the product was worked up as usual. 2:5-Dihydroxy-4-methoxy-6-methyl benzaldehyde crystallised from aqueous alcohol as yellow prisms melting at 162–63°.[2] Yield, 1·5 g. With alcoholic ferric chloride it gave a bluish green colour which slowly faded. It did not give any blue colour with concentrated nitric acid.

2:4:5-Trimethoxy-6-methyl benzaldehyde

The dihydroxy aldehyde (V) (1 g.) in acetone (75 c.c.) was refluxed for 12 hours with dimethyl sulphate (1·2 c.c.) and anhydrous potassium carbonate (6 g.). The product crystallised from water as colourless prisms melting at 103–04°.[2] It did not give any colour with ferric chloride solution (Found: C, 62·3; H, 6·9; $C_{11}H_{14}O_4$ requires C, 62·9; H, 6·7%).

Everninic acid (XI)

This was prepared according to the method of Robertson and Stephenson[13] by the oxidation of everninaldehyde as also by the hydrolysis of ethyl everninate with hot 15% sodium hydroxide solution.

Oxidation of everninic acid: isolation of para hydroxy-phenyl potassium sulphate (XII)

An ice-cold solution of everninic acid (XI) (6·0 g.) in aqueous sodium hydroxide (10%, 60 c.c.) was treated with aqueous potassium persulphate (8 g. in 150 c.c.) in small portions as in the previous experiments. After 24 hours, the solution was acidified to Congo-red and extracted with ether twice to remove the unreacted compound. An ether insoluble precipitate was also formed. It was filtered and recrystallised from hot water. The sulphate (XII) was thus obtained as colourless thin plates melting at 190–92° (decomp.). Yield, 2·5 g. It gave a deep blue colour with ferric chloride solution. A small portion was hydrolysed by warming with 2 N hydrochloric acid for 30 minutes on the water-bath and cooled. After removing the solid that separated, the filtrate was treated with barium chloride solution when a white precipitate was obtained indicating the presence of sulphate radical

(Found: C, 33·1; H, 4·0; $C_9H_9O_8SK$, H_2O requires C, 32·3; H, 3·3%). The aqueous solution left after the removal of the phenyl alkali sulphate did not yield any crystalline product on hydrolysis with concentrated hydrochloric acid.

2: 5-*Dihydroxy*-3-*methoxy toluene* (*IV*)

The above sulphate (XII) (1·0 g.) was suspended in 2 N hydrochloric acid (20 c.c.) and warmed in a water-bath at 50°. It rapidly went into solution with copious evolution of carbon dioxide. On cooling 2: 5-dihydroxy-3-methoxy toluene separated out. It crystallised from benzene as colourless long clusters of needles melting at 128–29°.[15] It did not give any colour with ferric chloride solution (Found: C, 62·3; H, 6·4; $C_8H_{10}O_3$ requires C, 62·3; H, 6·5%).

Methyl 2: 5-*dihydroxy*-4-*methoxy*-6-*methyl-benzoate* (*III*) (5-*hydroxy methyl everninate*)

The sulphate (0·3 g.) was esterified according to the general procedure of Saraiya and Shah,[16] by refluxing in acetone solution with methyl sulphate (0·13 c.c.) and sodium bicarbonate (1 g.) for 10 hours. The solvent was then distilled off and the residue was treated with 2 N hydrochloric acid (20 c.c.) and warmed at 80° for 30 minutes to effect the hydrolysis of the sulphate group. On cooling the methyl ester (III) separated which was crystallised from ethyl acetate. It formed colourless prisms melting at 153–54°.[2] It gave a bluish green colour with alcoholic ferric chloride, which rapidly faded (Found: C, 57·3; H, 5·8; $C_{10}H_{12}O_5$ requires C, 56·6; H, 5·7%).

The diacetate was prepared by refluxing (III) with acetic anhydride and pyridine. It crystallised from ethyl acetate-petroleum ether mixture as colourless leaflets melting at 169–70°[2] (Found: C, 57·0; H, 5·5; $C_{14}H_{16}O_7$ requires C, 56·7; H, 5·4%).

Methyl 2: 4: 5-*trihydroxy*-6-*methyl benzoate* (*XVII*) (5-*hydroxy methyl orsellinate*)

An ice-cold solution of methyl orsellinate (5·0 g.) in aqueous sodium hydroxide (10%, 60 c.c.) was treated with aqueous sodium persulphate (8·25 g. in 50 c.c.) in small portions with stirring. After 24 hours the solution was worked up as usual. Yield of XVII, 1 g. It crystallised from ethyl acetate (charcoal) as colourless hexagonal tablets melting at 204-05°.[2] Hiraiwa[17] recorded a melting point of 195°. The alcoholic solution gave a transient red colour with ferric chloride solution.

The triacetate prepared by refluxing with acetic anhydride and pyridine crystallised from ethyl acetate as colourless prisms melting at 146–47°.[2]

Methyl 2:3:4-trihydroxy-6-methyl-benzoate (3-hydroxy methyl orsellinate) (XXVII)

Methyl hæmatommate (2·1 g.) was dissolved in sodium hydroxide solution (25 c.c. of 2 N). To the cooled solution was added hydrogen peroxide (25 c.c. of 3%) dropwise with shaking. It was left at room temperature for 2 hours and then acidified with ice-cold dil. hydrochloric acid. The product was filtered and washed with water. Ether extraction of the filtrate gave some more of the substance. Yield, 0·9 g. It crystallised out of ethyl acetate as rectangular tablets and rods melting at 154–55°.[7] Its alcoholic solution gave a greenish blue colour with ferric chloride (Found: C, 49·7; H, 5·5; $C_9H_{10}O_5$, H_2O requires C, 50·0; H, 5·6%).

On acetylation with acetic anhydride and pyridine it yielded the triacetate which crystallised from ethyl acetate as stout rhombic prisms, melting at 120–21° (Found: C, 55·7; H, 4·9; $C_{15}H_{16}O_8$ requires C, 55·6; H, 4·9%).

Summary

Typical examples from lichen acids illustrating the applicability of the methods of para and ortho oxidation are studied. They follow the schemes of biogenesis given earlier and are found to proceed satisfactorily, thus providing convenient methods of synthesis. The common origin of CH_3, CH_2OH, CHO, and COOH and also of a hydroxyl group is emphasised.

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INDEX TO VOL. XXXV (A)

AUTHORS' INDEX

Agarwal, H. P. ..	*See* Doss and Agarwal.
Aghoramurthy, K. and Seshadri, T. R.	Nuclear oxidation in flavones and related compounds, XXXIX, 327.
Bagchi, Hari Das and Mukherjee, Bhola Nath	A note on the generalised Laguerre polynomial, 53.
Banerjee, D. P. ..	On the distribution of the range of variation of the ordered variates in samples of *n* from normal universe, 24.
Banerji, S. K. ..	Electricity of thunderstorms, 277.
Beri, R. M. ..	*See* Rao and Beri.
Bhagavantam, S. and Rao, T. Seshagiri	Elastic properties of polycrystalline aggregates, 129.
Bhatia, A. B. and Huang, K.	Note on the perturbation calculation of phase shifts for central and non-central interactions, 14.
Chakravorty, D. K., Mukerjee, S. K., Murty, V. V. S. and Seshadri, T. R.	Nuclear oxidation in flavones and related compounds, XXXV, 34.
Chandrasekhar, S. ..	The optical rotatory power of quartz and its variation with temperature, 103.
Dakshinamurti, C. ..	Role of ionic diffusion in the extraction of soil solutions, 314.
Deshpande, V. N. ..	*See* Jadhav and Deshpande.
Doss, K. S. G. and Agarwal, H. P.	The theory of redoxo-kinetic effect—a correction, 45.
Doss, K. S. G. and Kalyanasundaram, A.	Effect of surface active substances on the capacity of the electric double layer, 27.
..	Effect of pyridine on the reduction of oxygen in pulsating fields, 173.
Gakhar, K. L. ..	*See* Rao and Gakhar.
Gupta, K. K. ..	On the Fierz-Pauli equation for particles of spin 3/2, 255.
Gupta, S. R. and Seshadri, T. R.	A study of apiin from the parsley seeds and plant, 242.
Huang, K. ..	*See* Bhatia and Huang.

Iyengar, K. S. ..	Temperature dependence of ultrasonic velocity in liquid mixtures, 190.
Jadhav, G. V. and Deshpande, V. N.	Interaction of thionyl chloride and esters of aromatic hydroxy acids and their derivatives in presence of finely divided copper—IV, 114.
Jain, A. C. and Seshadri, T. R.	A new synthesis of menaphthone and lawsone, 233.
Kalyanasundaram, A. ..	*See* Doss and Kalyanasundaram.
Karandikar, R. V. ..	Measurements of atmospheric ozone and its vertical distribution at Kodaikanal (Lat. 10° 14′ N), 290.
Kartha, Gopinath ..	*See* Ramachandran and Kartha.
Mahajani, G. S., Tiruvenkatachar, V. R. and Thawani, V. D.	An application of Tschebyscheff polynomials to a problem in symmetric functions, 211.
Mukerjee, S. K. ..	*See* Chakravorty and others.
Mukerjee, S. K. and Seshadri, T. R.	Nuclear oxidation in flavones and related compounds, XXXVIII, 323.
Mukerjee, S. K., Seshadri, T. R. and Varadarajan, S.	Nuclear oxidation in flavones and related compounds, XXXVII, 82.
Mukherjee, Bhola Nath ..	*See* Bagchi and Mukherjee.
Mukherjee, B. N. and Nanjundiah, T. S.	Tschebyscheff polynomials $T_n(z)$ and $U_n(z)$ and functions of the second kind, 19.
Mukherjee, S. and Srivastava, H. C.	Action of acidic reagents on anhydro sugars, I, 178.
Murthy, A. R. Vasudeva and Rao, B. Sanjiva	Oxidation by Chloramine—T, I, II, 7, 69.
	The oxidation of hydrogen sulphide by potassium iodate, 99.
Murty, V. V. S. ..	*See* Chakravorty and others.
Nanjundiah, T. S. ..	*See* Mukherjee and Nanjundiah.
Narasimhachari, N. and Seshadri, T. R.	Components of the bark of *Prunus puddum*, II, 202.
Narasimhachari, N., Row, L. Ramachandra and Seshadri, T. R.	Nuclear oxidation in flavones and related compounds, XXXVI, 46
Narasimhamurty, T. S. ..	Maxwell effect in some simple organic liquids: comparison between theory and experiment, 126.
Neelakantam, K. and Viswanath, G.	A note on the determination of resacetophenone by Koppeschaar's method, 72.

Pandit, P. N., Tilak, B. D. and Venkataraman, K. — Anthraquinone and anthrone series, X, 159.

Puntambekar, S. V. .. — Chemical examination of the fatty oil from the seeds of *Mallotus philippinensis* Muel.-Arg., 57.

Radhakrishnan, T. .. — The optical properties of titanium dioxide, 117.

Ramachandran, G. N. and Kartha, Gopinath — X-Ray anti-reflections in crystals, 145.

Ramdas, A. K. .. — The thermo-optic behaviour of quartz, 89.

.. — The infra-red absorption spectrum of potassium chlorate crystals, I, 249.

Rangaswami, S. and Sastry, B. V. Rama — Chemical examination of plant insecticides, VI, 166.

Rao, B. Sanjiva .. — *See* Murthy and Rao.

.. — *See* Subrahmanya and others.

Rao, M. R. A. .. — *See* Subrahmanya and others.

Rao, P. S. and Beri, R. M. — Tamarind seed jellose: fermentative degradation, 1.

Rao, P. S. and Gakhar, K. L. — Studies on tuber hemicelluloses, I, 310.

Rao, T. Seshagiri .. — *See* Bhagavantam and Rao.

Row, L. Ramachandra .. — *See* Narasimhachari and others

Sastry, B. V. Rama .. — *See* Rangaswami and Sastry.

Sen Gupta, P. K. .. — The genesis and movement of the Nor'westers of Bengal, 303.

Seshadri, T. R. .. — *See* Chakravorty and others.

.. — *See* Narasimhachari and others.

.. — *See* Mukerjee and others.

.. — *See* Narasimhachari and Seshadri.

.. — *See* Jain and Seshadri.

.. — *See* Gupta and Seshadri.

.. — *See* Mukerjee and Seshadri.

.. — *See* Aghoramurthy and Seshadri.

Seshadri, T. R. and Varadarajan, S. — Insecticidal properties and chemical constitution, VI, 75.

Srinivasan, M. S. .. — Shortest semiregular continued fractions, 224.

Srivastava, H. C. .. — *See* Mukherjee and Srivastava.

Subrahmanya, R. S., Rao, M. R. A. and Rao, B. Sanjiva — A simple method for the study of variation of boundary tension with time, 136.

.. — Surface chemistry of congorubin solutions, 194.

Thawani, V. D. .. *See* Mahajani and others.
Thiruvenkatachar, V. R. .. *See* Mahajani and others.
Tilak, B. D. .. *See* Pandit and others.
Varadarajan, S. .. *See* Seshadri and Varadarajan.
.. *See* Mukerjee and others.
Venkataraman, K. .. *See* Pandit and others.
Venkiteshwaran, S. P. .. The F-type radio-meteorograph as an instrument to measure vertical currents in the atmosphere, 281.
Viswanathan, K. S. .. On the characteristic vibrations of linear lattices, 265.
Viswanath, G. .. *See* Neelakantam and Viswanath.

TITLE INDEX

Anthraquinone and anthrone series, X (Pandit and others), 159.

Apiin from the parsley seeds and plant, a study (Gupta and Seshadri), 242.

Atmospheric ozone and its vertical distribution at Kodaikanal (Lat. 10° 14′ N), measurements (Karandikar), 290.

Boundary tension, variation, with time, study, a simple method (Subrahmanya and others), 136.

Elastic properties of poly-crystalline aggregates (Bhagavantam and Rao), 129.

Electricity of thunderstorms (Banerji), 277.

Fierz-Pauli equation for particles of spin 3/2 (Gupta), 255.

F-Type radio-meteorograph as an instrument to measure vertical currents in the atmosphere (Venkiteshwaran), 281.

Ionic diffusion, role, in the extraction of soil solutions (Dakshninamurti), 314.

Infra-red absorption spectrum of potassium chlorate crystals, I (Ramdas), 249.

Insecticidal properties and chemical constitution, VI (Seshadri and Varadarajan) 75.

Insecticides, plant, chemical examination, VI (Rangaswami and Sastry), 166.

Laguerre polynomial, generalised, a note (Bagchi and Mukherjee), 53.

Linear lattices, characteristic vibrations (Viswanathan), 265.

Mallotus philippinensis Muel.-Arg., seeds, fatty oil, chemical examination. (Puntambekar), 57.

Maxwell effect in some simple organic liquids: comparison between theory and experiment (Narasimhamurty), 126.

Menaphthone and lawsone, a new synthesis (Jain and Seshadri), 233.

Nor'westers of Bengal, the genesis and movement (Sen Gupta), 303.

Nuclear oxidation in flavones and related compounds, XXXV (Chakravorty and others), 34; XXXVI (Narasimhachari and others), 46; XXXVII (Mukherjee and others), 82; XXXVIII (Mukerjee and Seshadri), 323; XXXIX (Aghora - murthy and Seshadri), 327.

Optical properties of titanium dioxide (Radhakrishnan), 117.

Optical rotatory power of quartz and its variation with temperature (Chandrasekhar), 103.

Oxidation by chloramine-T, I, II (Murthy and Rao), 7, 69.

Oxidation of hydrogen sulphide by potassium iodate (Murthy and Rao), 99.

Perturbation calculation of phase shifts for central and non-central interactions note (Bhatia and Huang), 14.

Prunus puddum, bark, components, II (Narasimhachari and Seshadri), 202.

Pulsating fields, reduction of oxygen, effect of pyridine (Doss and Kalyanasundaram), 173.

Redoxo-kinetic effect, theory—a correction (Doss and Agarwal), 45.

Resacetophenone, determination, by Koppeschaar's method, a note (Neelakantam and Viswanath), 72.

Semiregular continued fractions, shortest (Srinivasan), 224.

Sugars, anhydro, acidic reagents, action, I (Mukherjee and Srivastava), 178.

Surface active substances, effect, on the capacity of the electric double layer (Doss and Kalyanasundaram), 27.

Surface chemistry of congorubin solutions (Subrahmanya and others), 194.

Tamarind seed jellose: fermentative degradation (Rao and Beri), 1.

Thermo-optic behaviour of quartz (Ramdas), 89.

Thionyl chloride and esters of aromatic hydroxy acids and their derivatives in presence of finely divided copper, interaction, IV, 114.

Tschebyscheff polynomials, an application, to a problem in symmetric functions (Mahajani and others), 211.

Tschebyscheff polynomials $T_n(z)$ and $U_n(z)$ and functions of the second kind (Mukherjee and Nanjundiah), 19.

Tuber hemicelluloses, studies, I (Rao and Gakhar), 310.

Ultrasonic velocity in liquid mixtures, temperature dependence (Iyengar), 190.

Variates, ordered, distribution of the range of variation, in samples of n from normal universe (Banerjee), 24.

X-Ray anti-reflections in crystals (Ramachandran and Kartha), 145.